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SAFETY STUDIES ON Li/SOCl₂ RESERVE BATTERY

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The effects of cell design and metal-phthalocyanine catalysts on the safety of Li/SOCl₂ reserve cells were evaluated. Cathode-limited design cells either vented or exploded during forced overdischarge. Both forced overdischarge current density, and overdischarge time into reversal influenced the cell failure unpredictably. Anode-limited design cells, on the other hand, generated severe internal heat during reversal, but sustained higher forced overdischarge current densities than cathode-limited design cells without either venting or exploding. When the 1.5M LiAlCl₄/SOCl₂ was

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20. Abstract

replaced with 1.5M $LiAlCl_4/SO_2Cl_2$ electrolyte in the cathode-limited design cells, both the cell discharge life and cell safety improved.

The catalyst stability and stainless steel (bellow material) compatibility were also studied in both neutral and acidic electrolytes. The catalyst was found to be stable and the stainless steel specimens (316L and 321) experienced only surface corrosion after 12-month storage. The surface film formed during the initial surface corrosion appeared to inhibit further corrosion.

Heat cool cycles between -40 and 71^6C of fresh cells and partially or fully discharged D-cells did not adversely influence the cell pressure at the end of 100% depth of discharge.

Acknowledgement

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FIGURES

FIGURES - cont'd

TABLES

1.0 INTRODUCTION

Safe performance of the lithium-thionyl chloride (1-3) electrochemistry is important if it is to become a viable candidate for potential Navy applications. Some of the safety hazards associated with the system under various conditions have hindered its acceptability despite its many superior performance characteristics. The widely accepted reaction mechanism,

$$SOCl_2 + 2\bar{e} \longrightarrow 2\ Cl^- + \frac{1}{2}S + \frac{1}{2}SO_2$$
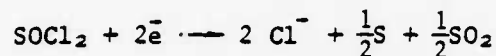
is not fully understood. The intermediate reaction species generated by chemical and electrochemical reactions are not identified fully.

Recent studies (4,5) on electrocatalytic reduction of $SOCl_2$ indicate possible reactions involving destabilization of intermediate reduction species via further fast electrochemical reduction and/or modification of the overall reduction mechanism. Thus, at the catalyzed cathode surfaces, the reaction mechanism is simplified resulting in a safer $Li/SOCl_2$ system.

The broad objective of this program is to define, understand, and seek out solutions for the safety problems associated with reserve $Li/SOCl_2$ cells/batteries. Both catalyzed and uncatalyzed cathodes are used in these studies. The two catalysts selected are electrolyte-soluble iron phthalocyanine, FePc, and electrolyte-insoluble polymeric cobalt phthalocyanine $(CoPc)_n$. Of these, FePc has the best catalytic activity for reduction of $SOCl_2$ in reserve systems. However, even though $(CoPc)_n$ has lower catalytic activity than FePc, its insolubility makes it a better candidate for active batteries and reserve batteries requiring long discharge life.

Cell design, whether catalyzed or not, is the primary influence on safety of $Li/SOCl_2$ cells/batteries. Both electrode design and electrolyte management are significant factors; specific program objectives were therefore to:

- Determine cell internal pressure characteristics at various discharge depths over a wide range of temperatures. This provides the needed data for vent design at both the cell and battery levels.

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- Evaluate long term reservoir storage capability with and without catalyst.

- Evaluate the effect of electrode design (anode-limited vs cathode-limited) on safety during forced overdischarge into reversal, with and without $(CoPc)_n$ catalyst.

- Elucidate reaction mechanisms and identify intermediate reactive species.

2.0 INTERNAL CELL PRESSURE CHARACTERISTICS

Internal cell pressure is one of the uncertain safety factors associated with $Li/SOCl_2$ systems under a variety of use and abuse conditions, and significantly impacts the design approach for safety vents in $Li/SOCl_2$ hardware. In the $Li/SOCl_2$ system, internal cell pressure increases with storage temperature and time, the extent depends upon depth of discharge. Standard D-size cells, equipped with pressure transducers, were used to measure this pressure response. These data can be used to aid in designing safety vents for $Li/SOCl_2$ reserve batteries. A total of eight cells were built to accomplish this task. Four of these cells contained $(CoPc)_n$ catalyzed cathodes; the reaminder were built with uncatalyzed baseline cathodes.

CELL COMPONENTS

- **Anode**

A 0.020" thick lithium foil (Foote Mineral Company) was used, with two pieces sandwiched around a 316L stainless steel current collector. The physical data of the anodes were:

Dimensions:	1.75" x 6" x 0.020"
Area:	135.5 cm^2
Weight (of lithium):	3.676g
Anode Capacity:	3.676 grams x 3.86 Ah/gram (theoretical)
	= 14.19 Ah

- **Cathode**

All cathodes were fabricated via the process described in Figure 1. Baseline cathodes contained 100% compressed-grade Shawinigan acetylene black (SAB) and Teflon-6 binder in a 95/5 weight percent ratio. The $(CoPc)_n$ catalyzed cathode composition was 90% SAB, 5% catalyst and 5% Teflon-6 binder. Two cathode pads were pressed on either side of a 316L stainless steel current collector.

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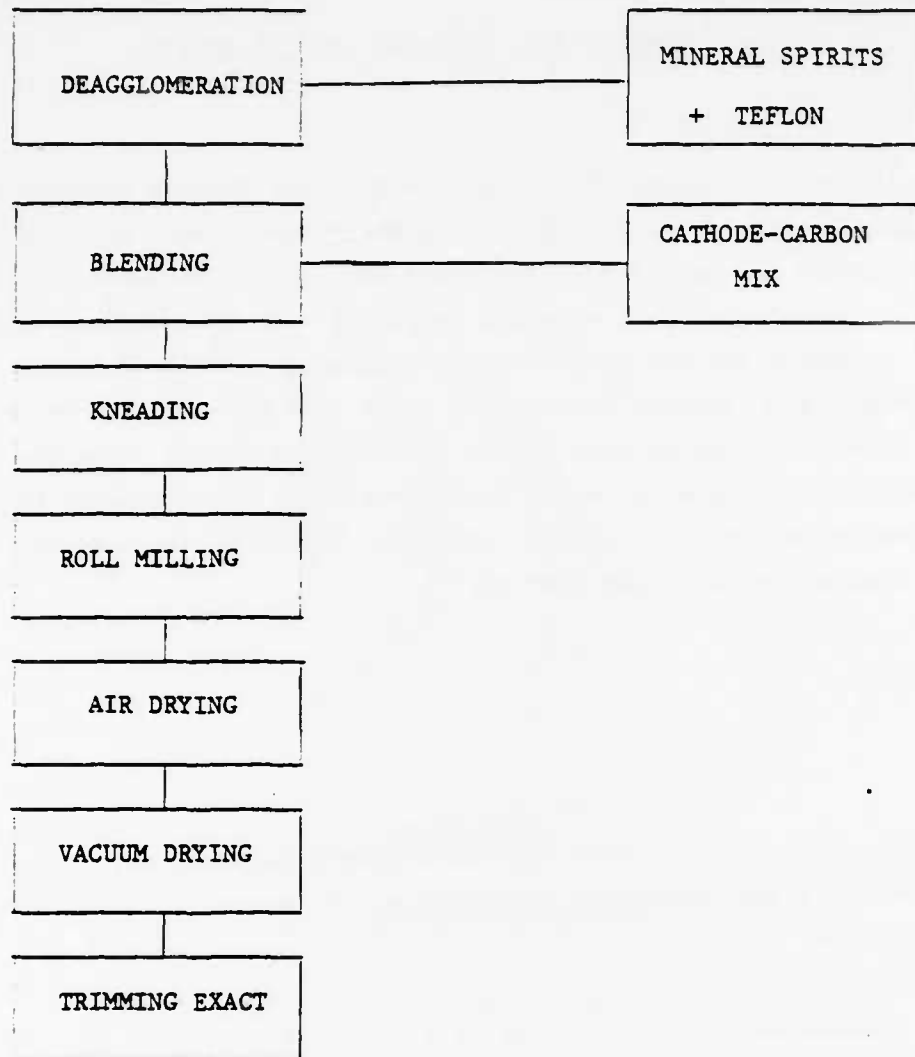
Figure 1. Flow Diagram of Cathode Fabrication Process. Workability of the process not restricted to specific carbon type. Rolling incurs excellent mechanical integrity on the cathode.

The physical characteristics of the cathode pads were:

Dimensions: 1.75" x 8" x 0.040" (one piece)
                1.75" x 9" x 0.040" (second piece)

Baseline Cathode

Total Cathode Area: 192.0 cm^2
Total Weight of Cathode: 6.94 g
Volume: 19.501 ml
Density: 0.356 g/ml
Carbon Volume: (95 x 6.94 ÷ 1.95) ÷ 100 = 3.381 ml
Teflon Volume: (5 x 6.94 ÷ 2.2) ÷ 100 = 0.258 ml
∴ Total solid volume of cathode: 3.381 + 0.158 = 3.539 ml
Void space in the cathode: 19.501 - 3.539 = 15.962 ml
Porosity: (15.962 ÷ 19.501) x 100 = 81.85%
Projected Cathode Capacity: 6.94 grams x 1.75 Ah/gram = 12.14 Ah

Catalyzed Cathode

Total Cathode Area: 192.0 cm^2
Total Weight of Cathode: 7.31 g
Cathode Volume: 19.501 ml
Density: 0.375 g/ml
Carbon Volume: (90 x 7.32 ÷ 1.95) ÷ 100 = 3.374 ml
Teflon Volume: (5 x 7.31 ÷ 2.2) ÷ 100 = 0.166 ml
Catalyst Volume: (5 x 7.31 ÷ 2.2) ÷ 100 = 0.116 ml
    (Catalyst Density estimated to be 2.2 g/   )

Total Solid Volume: 3.374 + (0.166 x 2) = 3.706 ml
Void space in the cathode: 19.501 - 3.706 = 15.795 ml
Porosity: 15.795 ÷ 19.501 = 81%
Projected Cathode Capacity: 7.31 grams x 2.0 Ah/gram = 14.62 Ah

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- <u>Separator Material</u>

Non-woven glass mat separators, manufactured by the Manning Paper Company, were used. The physical data were:

Dimensions:	2" x 11" x 0.005"
Area:	141.94 cm^2 (each side)
Volume:	1.802 ml
Weight:	0.432 g
Porosity:	90%
Solid Volume:	$\frac{1.802 \times 10}{100} = 0.180$ ml
Void Space:	1.622 ml

- <u>Current Collector</u>

Stainless steel 316L current collector grids and leads (Lancaster Manf. Co., PA) were used for both anode and cathode. The selection of 316L stainless steel was based on the fact that this same material was being used under Contract N60921-81-C-0351, supported by NSWC.

Anode Grid Dimensions:	1.6" x 5.5" x 0.010"
Weight:	1.318 g
Cathode Grid Dimensions:	1.6" x 7.5" x 0.010"
Weight:	1.688 g
Volume:	1.966 ml
Density of Grid:	$1.688 \div 1.966 = 0.8586$ g/ml
Density of 316L SS:	8.00 g/ml
$\therefore$ Solid Volume of Grid:	$(0.85686 \times 1.966) \div 8.0 = 0.211$ ml
Void Space:	$1.966 - 0.211 = 1.755$ ml

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●   Insulators

Tefzel sheets, 0.005" thick and 1.27" in diameter, were used at both top and
bottom of the electrode wrap as insulators. The top insulator had a 0.10"
slit slightly off center through which the anode lead passed.

D-cell cans (316L S.S.), terminal plates, grids and leads were cleaned in
methyl ethyl ketone (MEK) before use. Leads were spot welded to current collectors,
the cathode lead was spot welded to the cell case, the anode lead was spot
welded to the center pin, and the cell was closed by laser welding the terminal
plate to the cell case.

EFFECT OF INTERMITTENT DISCHARGE ON CELL PRESSURE

Four D-cells, two with baseline cathodes and two with $(CoPc)_n$ catalyzed cathodes,
were activated by vacuum fill technique. In each cell, 28 ml of 1.5M $LiAlCl_4/SOCl_2$
electrolyte was added to fill up the void space in the electrode stack. The
theoretical capacity of the electrolyte was approximately 21 amp-hours. Thus,
the cell was insured of flooded condition throughout its life since the maximum
theoretical output of the cell design was 14.2 Ah based on lithium weight.

After activation the cells were allowed to stand at ambient temperature for
6 hours and then they were placed in an environmental chamber built by Tenney
Engineering, Inc., New Jersey. This chamber, Model #BTR, was equipped with a
programmable memory for heat-cool cycles and a battery backed power to protect
the memory in case of electrical failure. For the present study, the chamber
was programmed to cool down to $-40^{\circ}C$ from ambient temperature in two hours
and then start heat-cool cycles. During these cycles, the temperature was
programmed to increase or decrease by $11^{\circ}C$ and come to equilibium. A total
of 45 minutes was allowed for each change in temperature. For each heat-cool
cycle between -40° and $71^{\circ}C$, a total of 15 hours was required.

Fresh cells were subjected to six heat-cool cycles. A small increase in pressure
between 38° and $71^{\circ}C$ was observed after six cycles. However, no hysterises
between pressure and temperature were observed.

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These cells were then discharged to approximately 50% depth of discharge at a constant current of 0.192A (1 mA/cm^2), after which six heat-cool cycles were carried out. In Figures 2 and 3, the relationship between pressure and temperature for the first and the last cycle is shown. It should be noted that the pressure values were not corrected for the void space in the pressure transducer. No significant differences were found between catalyzed and uncatalyzed cells. During heat-cool cycles, the small hysterises recorded could be attributed to the insufficient time allowed to reach equilibrium temperatures.

After heat-cool cycles, the above cells were further discharged to 0.7 volts and then subjected again to six more heat-cool cycles. In Figures 4 and 5, the pressure-temperature behavior is plotted for the first and sixth cycle. Since the pressure values were not corrected for the extra void space due to pressure transducer and valve, the pressure in an actual D-cell will be higher than reported in Figures 1-5. Actual cell pressure at $71^{o}C$ is expected to be approximately 100 psi for both catalyzed and uncatalyzed cells.

The discharge characteristics and the pressure of cells with dept of discharge are plotted in Figure 6 and 7. The cell with the catalyzed cathode showed nearly 150 mV higher voltage than the one with an uncatalyzed cathode. However, the cell life and pressure were not significantly effected by $(CoPc)_n$ catalyzed cathodes at the low current discharge rate of 1 mA/cm^2.

EFFECT OF CONTINUOUS DISCHARGE ON CELL PRESSURE

In order to check if any chemical changes took place when the cells were subjected to heat-cool cycles after each depth of discharge, four fresh D-cells were 100% discharged and then were subjected to heat-cool cycles. The discharge characteristics along with the internal pressure of cells with baseline cathodes (two cells) and $(CoPc)_n$ cathodes (two cells) are given in Figures 8 and 9, respectively. The cell pressures reported in Figures 8 and 9 are the corrected values for the void space due to pressure transducer and the valve attachments. The pressure levels at the end of discharge for this mode of continuous discharges are, for practical purposes, the same as the ones that were intermittently heated and cooled (See Figures 6 and 7).

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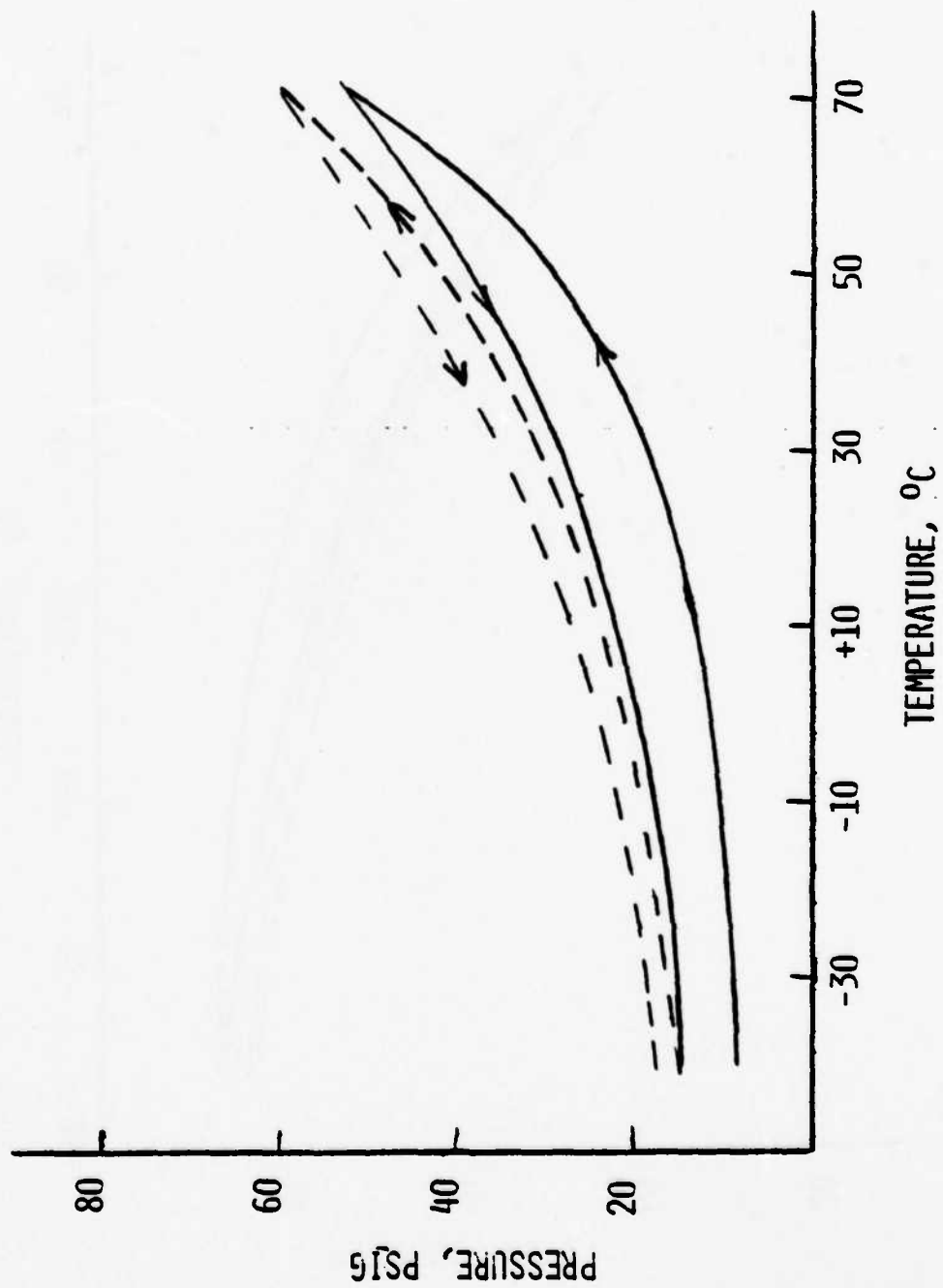
FIGURE 2. HEAT-COOL CYCLES OF Li/SOCl₂ D-CELL WITH 1.5M LiAlCl₄/SOCl₂ ELECTROLYTE AFTER 41% DEPTH OF DISCHARGE. — FIRST CYCLE. --- SIXTH CYCLE.

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FIGURE 3. HEAT-COOL CYCLES OF Li/SOCl$_2$ D-CELL WITH (CoPc) CATALYZED CATHODE AND 1.5M LiAlCl$_4$/SOCl$_2$ ELECTROLYTE AFTER 45% DEPTH OF DISCHARGE. - FIRST CYCLE, --- SIXTH CYCLE.
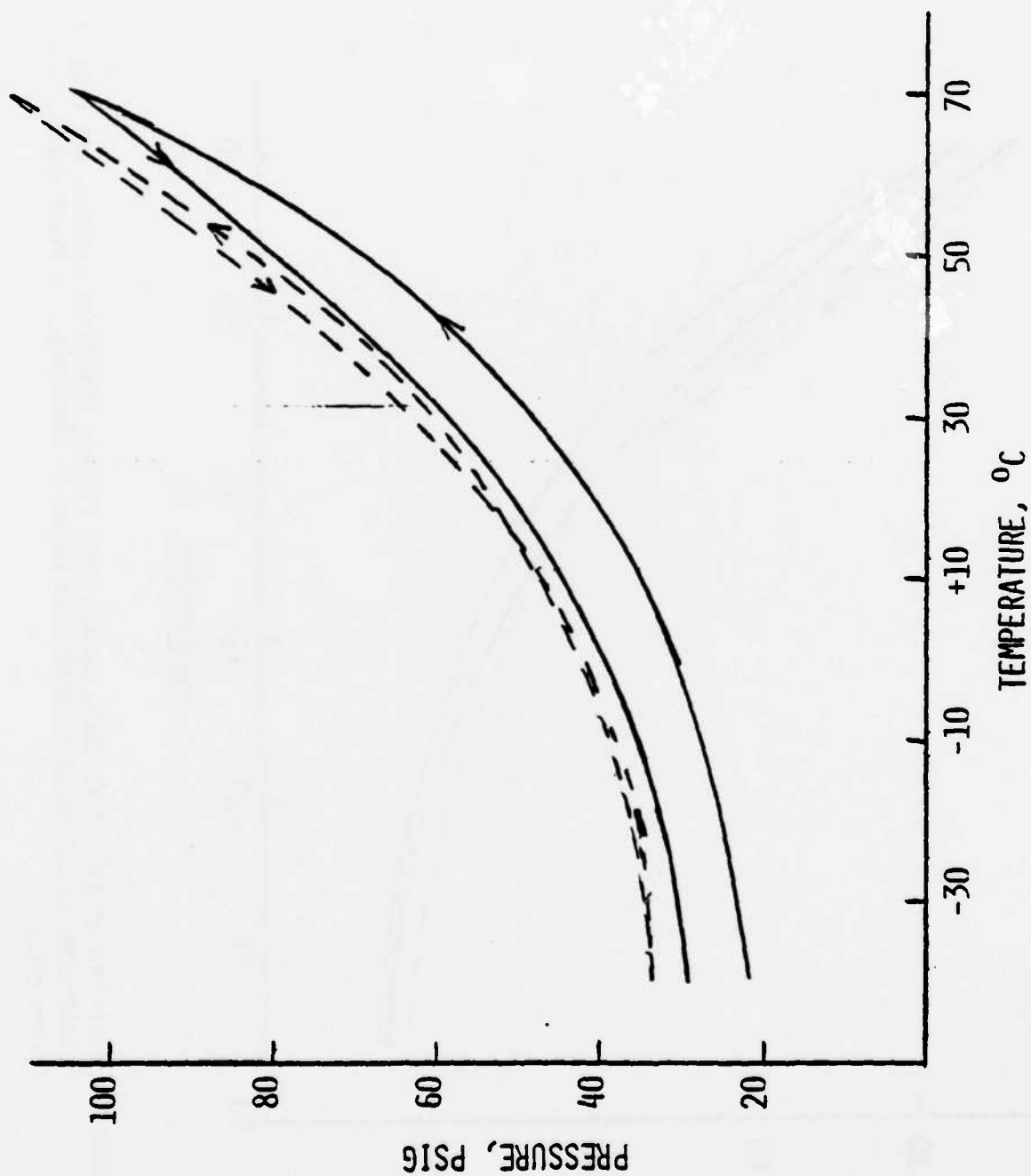
FIGURE 4. HEAT-COOL CYCLES OF Li/SOCl₂ D-CELL WITH 1.5M LiAlCl₄/SOCl₂ ELECTROLYTE AFTER 100% DEPTH OF DISCHARGE. — FIRST CYCLE, --- SIXTH CYCLE.

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FIGURE 5. HEAT-COOL CYCLES OF Li/SOCl$_2$ D-CELL WITH (CoPc) CATALYZED CATHODE AND 1.5M LiAlCl$_4$/SOCl$_2$ ELECTROLYTE AFTER 100% DEPTH OF DISCHARGE. - FIRST CYCLE, ---- SIXTH CYCLE

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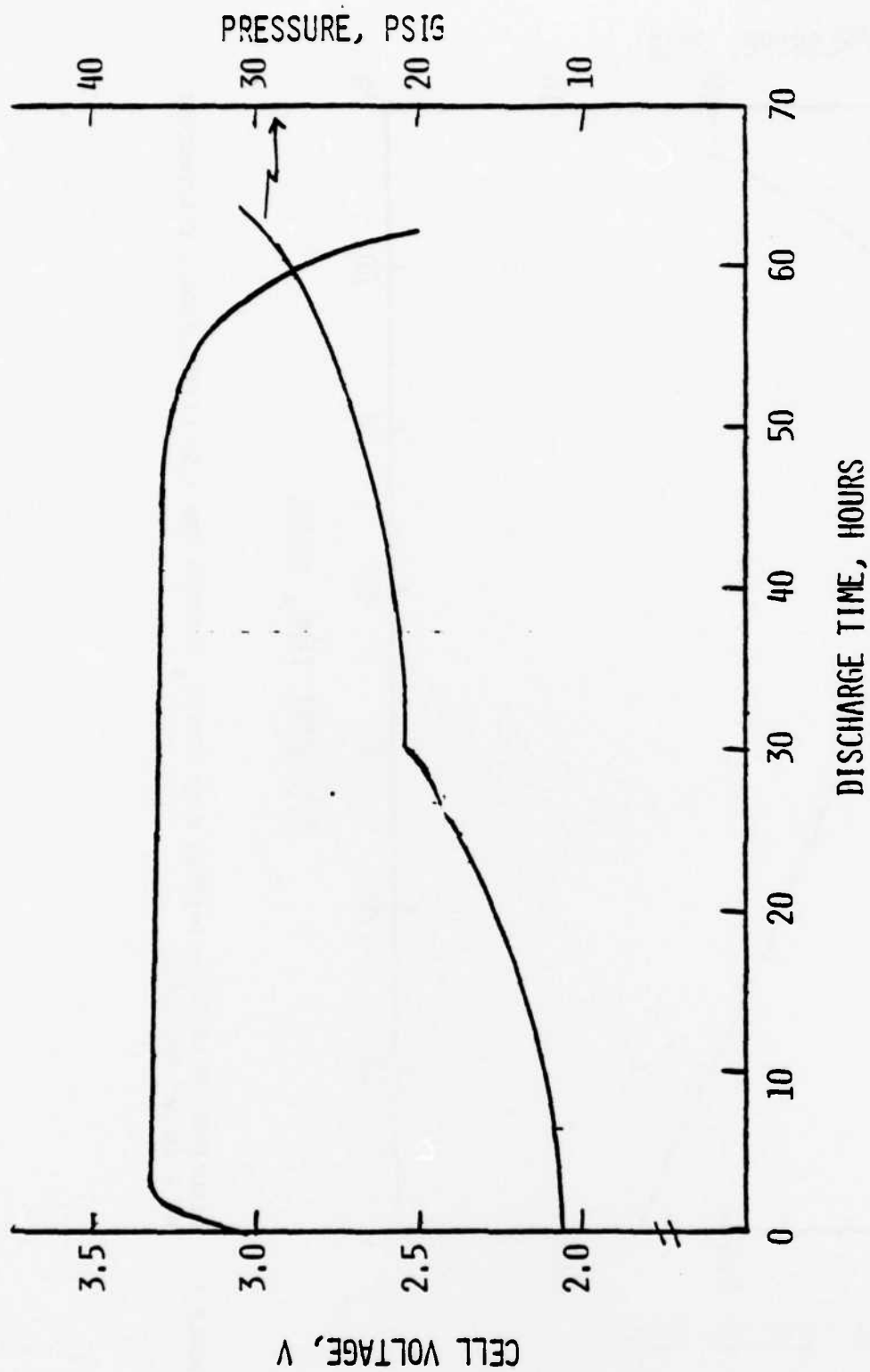
FIGURE 6. DISCHARGE OF Li/SOCl$_2$ D-CELLS WITH 1.5M LiAlCl$_4$/SOCl$_2$ ELECTROLYTE AT 1 mA/cm^2 AND 23°C.

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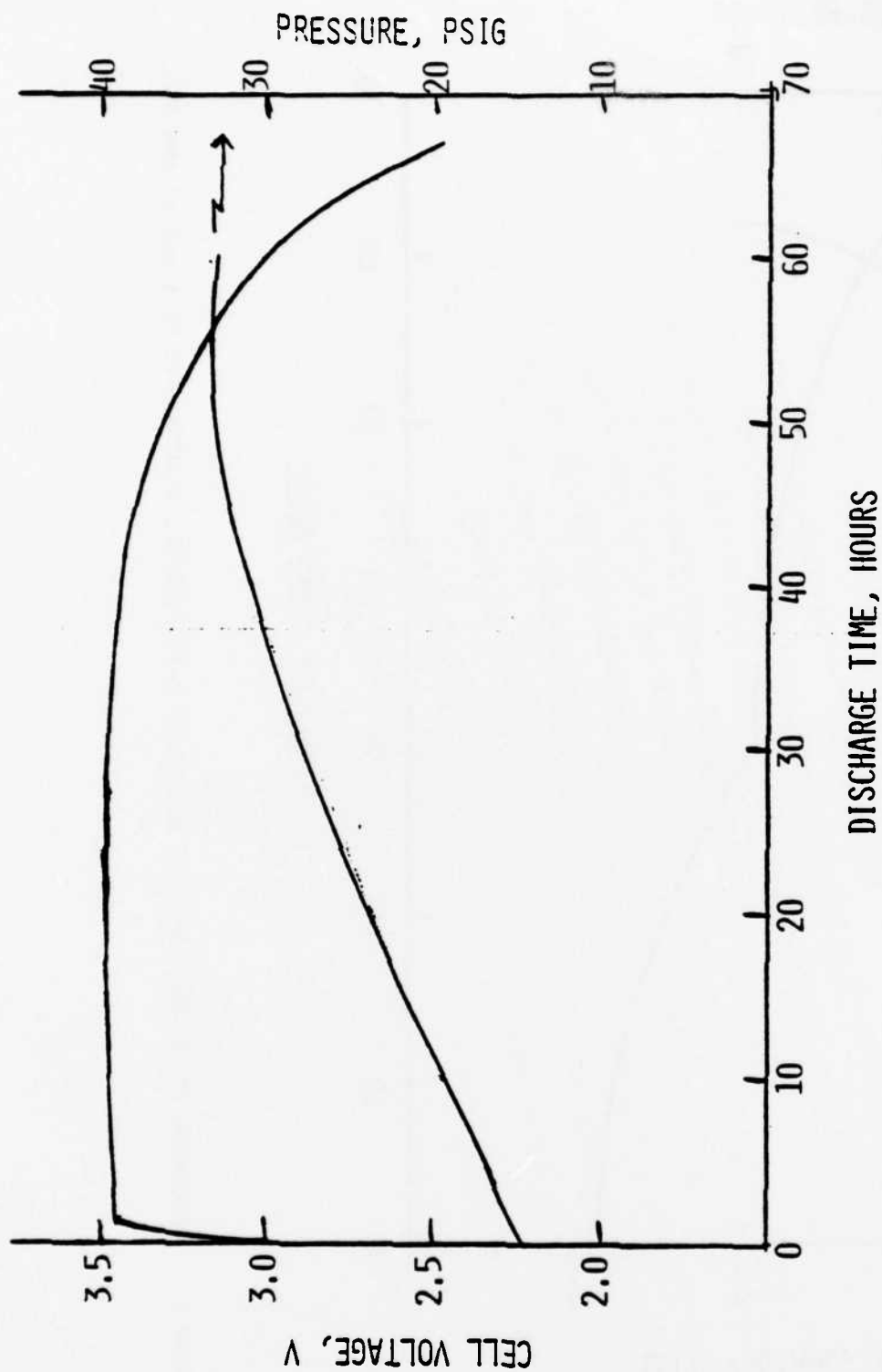
FIGURE 7. DISCHARGE OF LI/SOCL₂ D-CELLS WITH (CoPc)ₙ CATHODE AND 1.5M LiAlCl₄/SOCl₂ ELECTROLYTE AT 1 mA/cm² AND 23°C.

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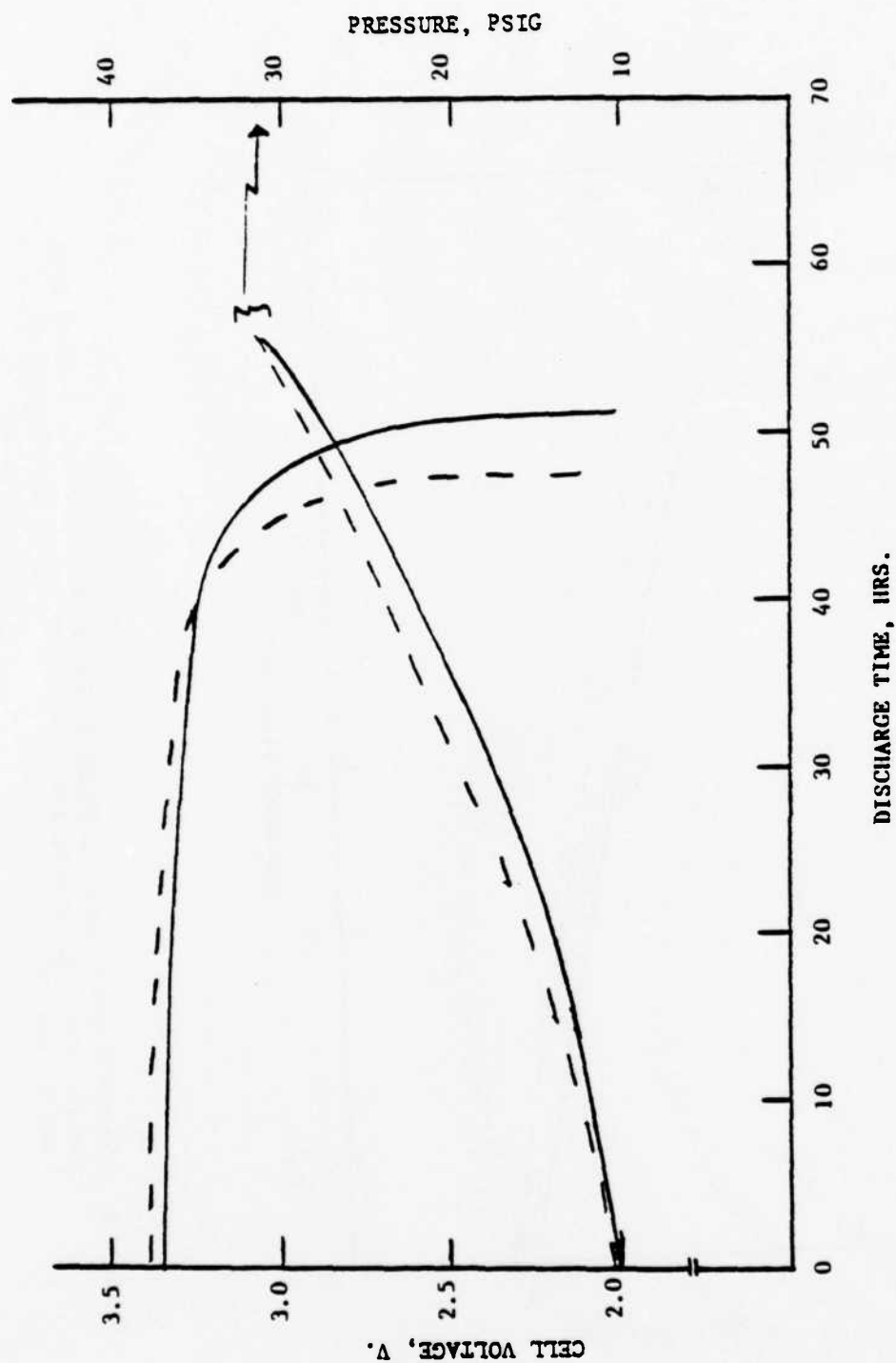
FIGURE 8. DISCHARGE PERFORMANCE AND PRESSURE BEHAVIOR OF Li/SOCl$_2$ D-CELLS WITH POROUS CARBON CATHODE AND 1.5M LiAlCl$_4$/SOCl$_2$ ELECTROLYTE AT 1 mA/cm^2 AND 23°C.

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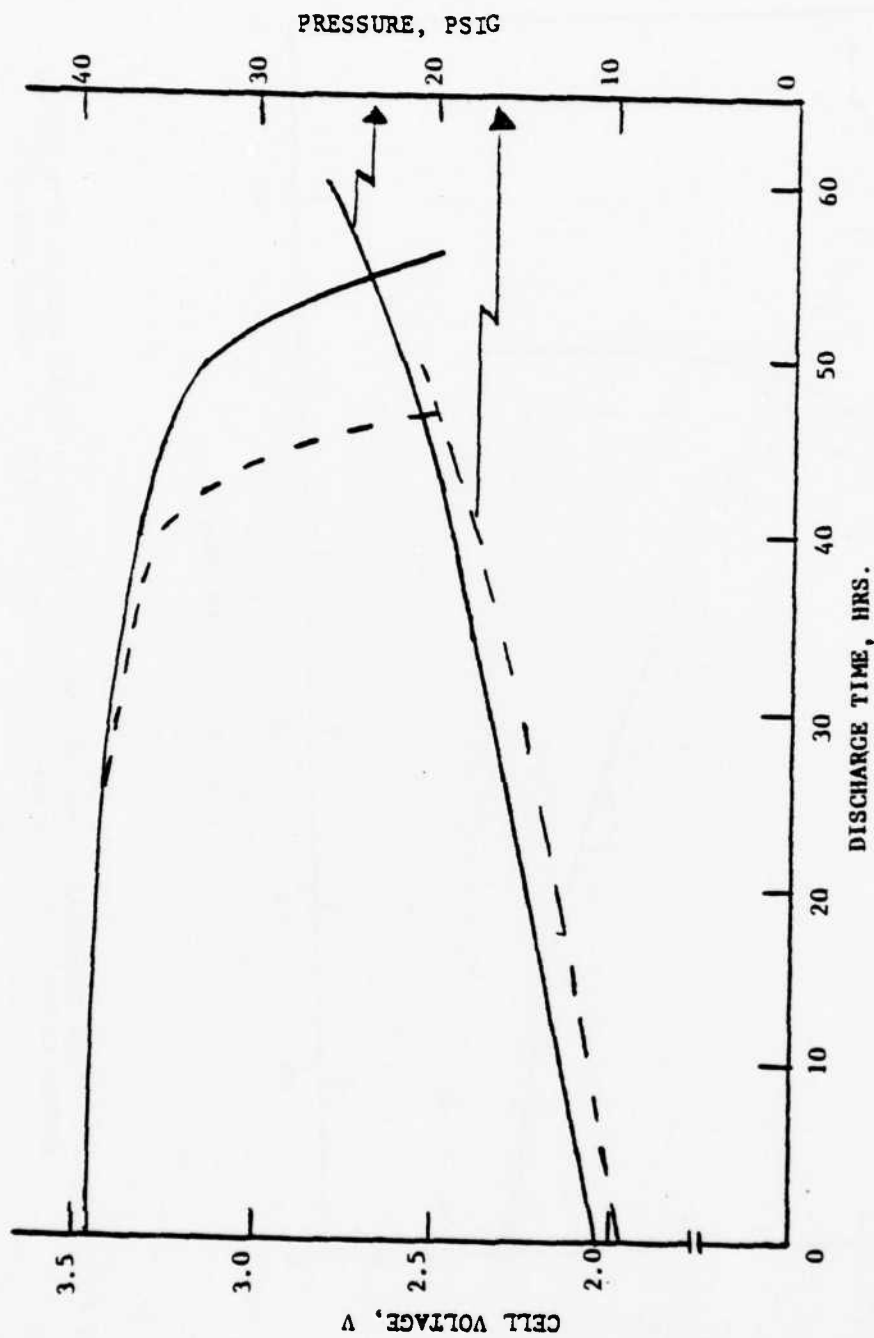
FIGURE 9. DISCHARGE PERFORMANCE AND PRESSURE BEHAVIOR OF Li/SOCl$_2$ D-CELLS WITH (CoPc)$_n$ CATALYZED CATHODE AND 1.5M LiAlCl$_4$/SOCl$_2$ ELECTROLYTE AT 1 mA/cm^2 AND 23°C.

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The four D-cells after 100% depth of discharge were subjected to heat-cool
cycles. In Figures 10 and 11, the pressure-temperature hysteresis of these
cells are given. Again, no severe deviation was observed from the behavior
found in cells which were subjected to several heat-cool cycles at various
depths of discharge shown in Figures 4 and 5. The maximum pressure buildup
under normal discharge conditions (100% DoD to 0.0 volts) is less than
100 psig.
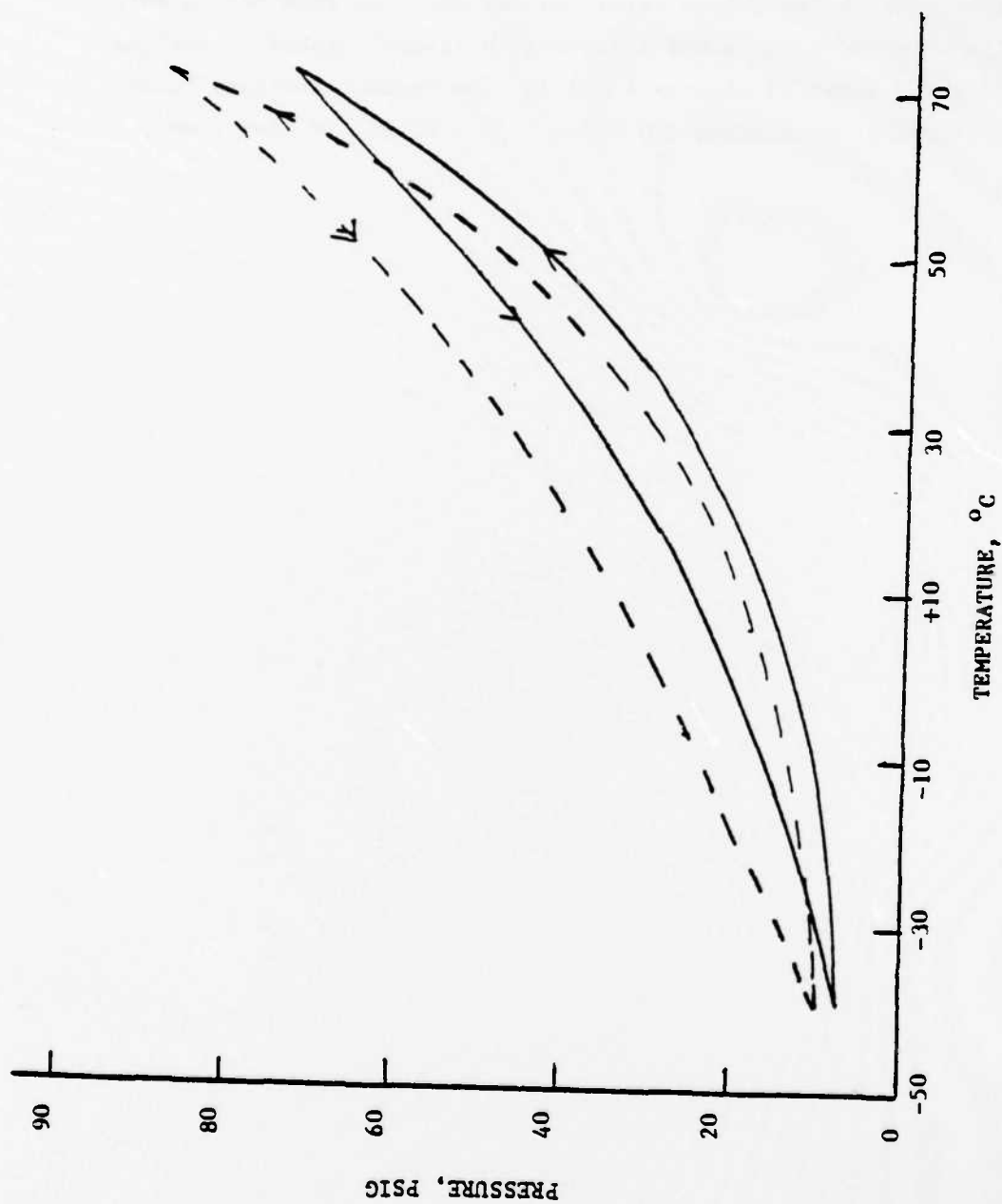
FIGURE 10. HEAT-COOL CYCLES OF Li/SOCl₂ D-CELL WITH BASELINE CATHODE AND
1.5M LiAlCl₄/SOCl₂ ELECTROLYTE AFTER 100% DEPTH OF DISCHARGE AT A CONSTANT
(CONTINUOUS) DISCHARGE OF 1 mA/cm². FIRST CYCLE ———, SIXTH CYCLE ———

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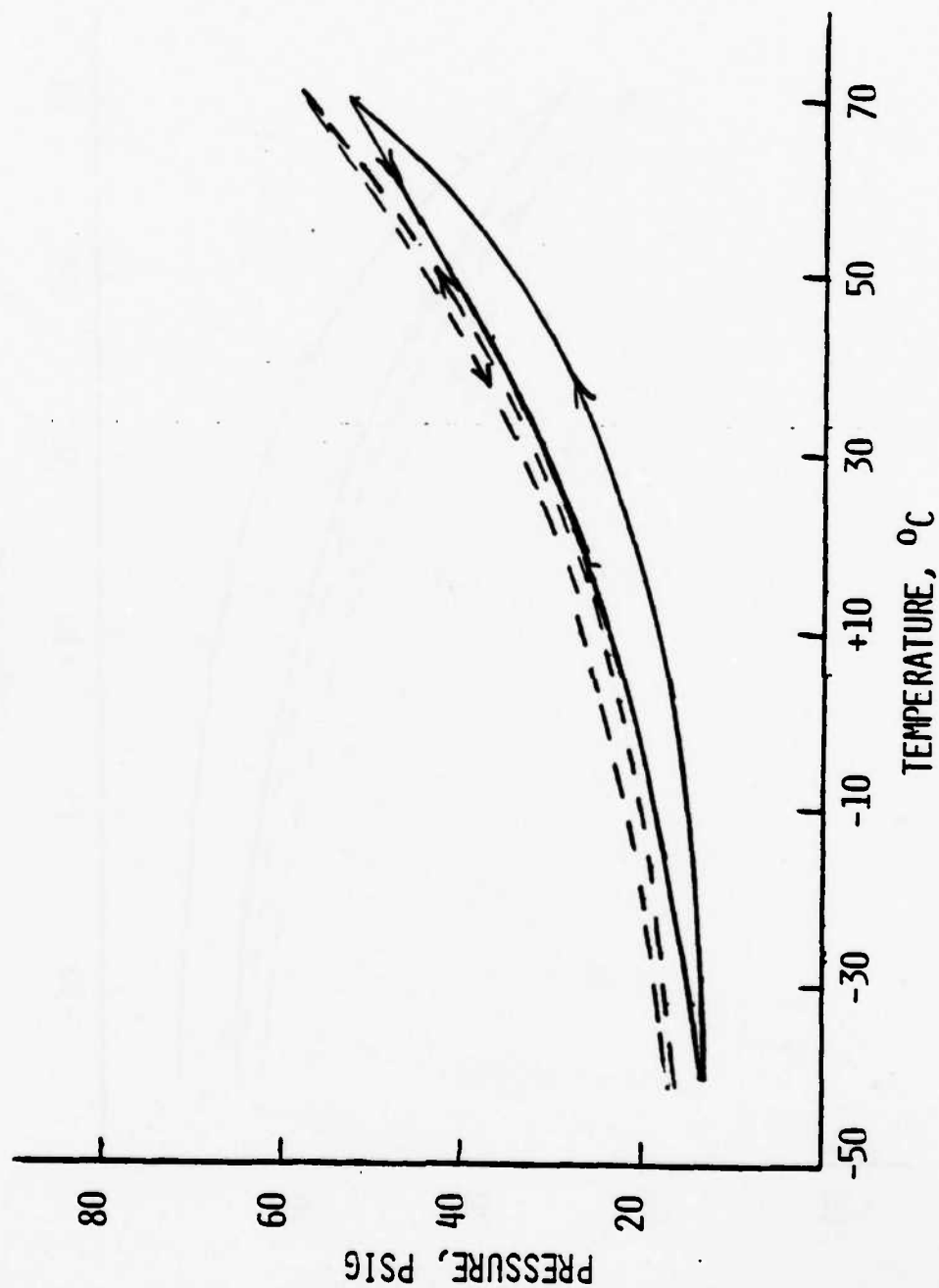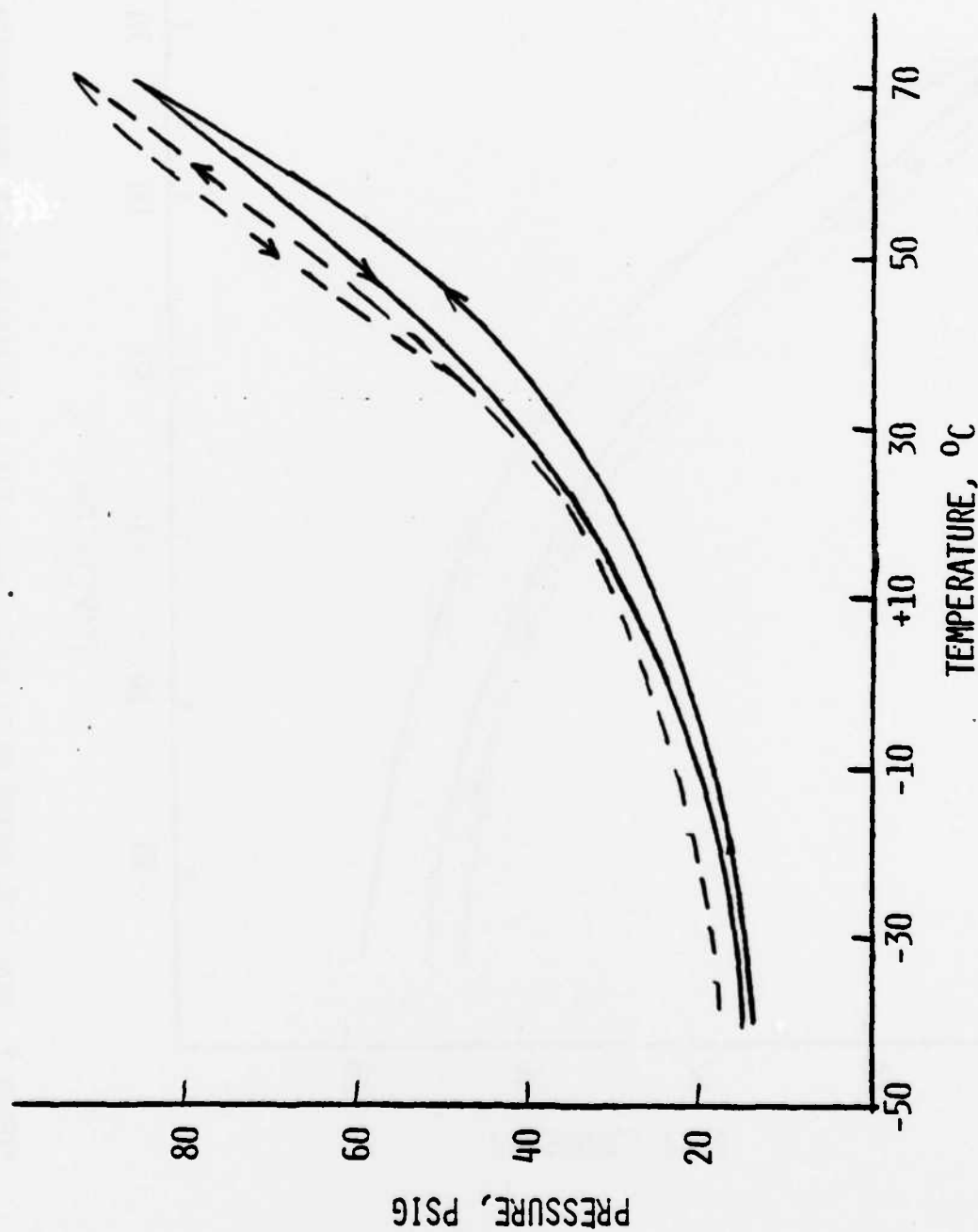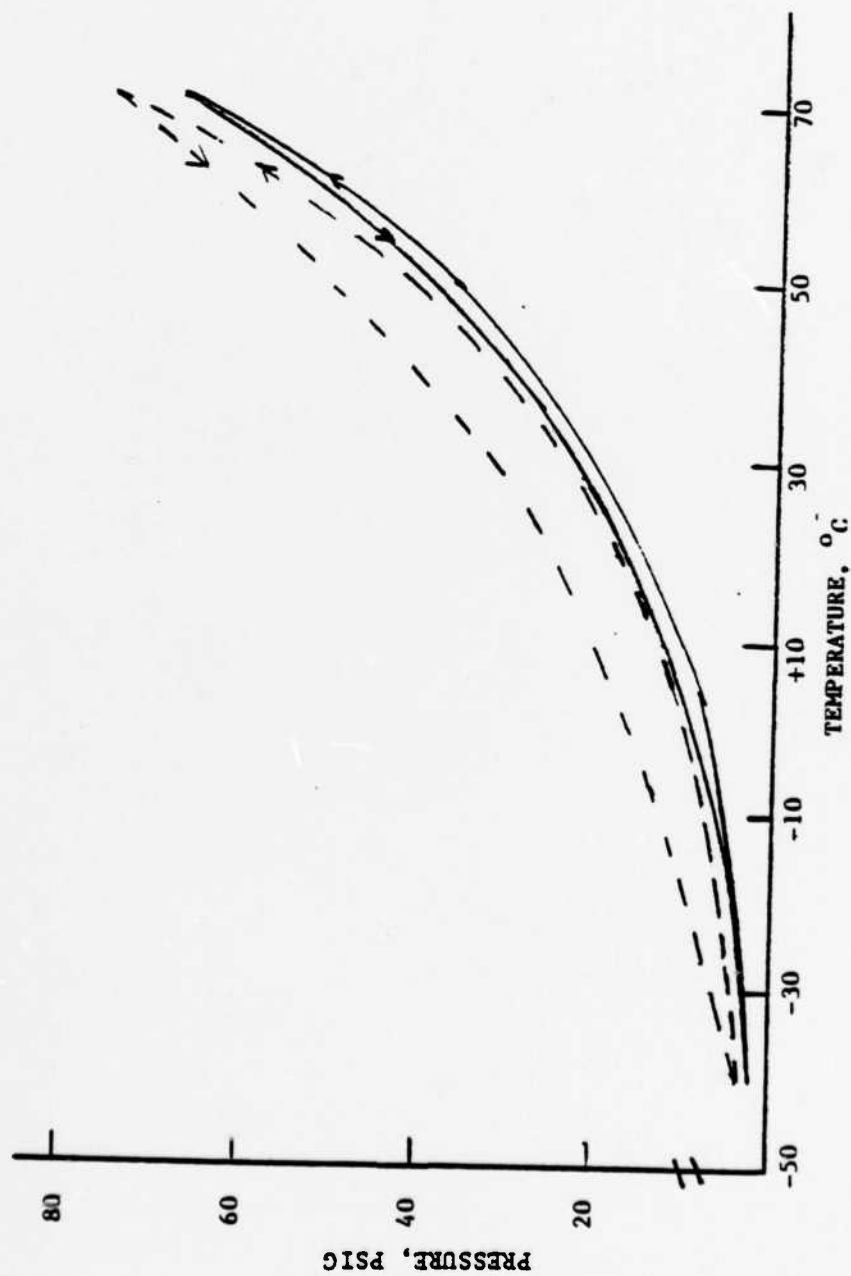FIGURE 11. HEAT-COOL CYCLES OF $Li/SOCl_2$ D-CELL WITH (CoPc) CATALYZED CATHODE AND 1.5M $LiAlCl_4/SOCl_2$ ELECTROLYTE AFTER 100% DEPTH OF DISCHARGE AT A CONSTANT CURRENT (CONTINUOUS) DISCHARGE OF 1 mA/cm^2. FIRST CYCLE ———, SIXTH CYCLE ———.

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3.0 LONG TERM RESERVOIR STORAGE CAPABILITY

Stainless steels in the 300 series are commonly used in $Li/SOCl_2$ batteries for hardware parts. The popular acceptance of 316L stainless steel is mostly based on its apparent compatibility with $LiAlCl_4 \cdot SOCl_2$ electrolyte in active primary cells, but no systematic evaluation of its long term storage compatibility with electrolyte for reserve batteries, which require several years of storage, has been carried out.

In this program, the compatibility of both 316L and 321 stainless steel in neutral and acidic electrolytes was evaluated. Stability of the polymeric cobalt phthalocyanine catalyst and its corrosivity effect on 316L and 321 S.S. were also examined in a neutral electrolyte environment.

Glass ampuls were selected to store the electrolyte according to the storage test plan shown in Table 1 and 2. The electrolytes were 1.5M $LiAlCl_4 \cdot SOCl_2$ and (0.5M $LiAlCl_4$ + 2.3M $AlCl_3$)$SOCl_2$. (Acidic electrolyte was included because of the potential application by the Navy for higher rate reserve batteries).

Table 1. Test Plan and Ampul Preparation

Group A	1.5M $LiAlCl_4/SOCl_2$ and $(CoPc)_n$ catalyst
Group B	" and 321 stainless steel
Group C	" and 316L stainless steel
Group D	2.3 M $AlCl_3$ + 0.5M $LiAlCl_4/SOCl_2$ and 321 stainless steel
Group E	" " and 316L stainless steel
Group F	1.5M $LiAlCl_4/SOCl_2$ and 321 stainless steel and $(CoPc)_n$ catayst
Group G	" and 316L stainless steel & $(CoPc)_n$ catalyst

The sealed ampuls with catalyst (Group F & G) and without catalyst (Group B, C, D and E) were stored at $32^{\circ}C$ and $71^{\circ}C$, respectively. Group A ampuls were stored at ambient temperature. In reserve battery applications for the Navy, the maximum operating temperature is $32^{\circ}C$. Since the catalyst is a part of the cathode

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Table 2. Evaluation of Stainless Steel Specimen Compatibility in 1.5M LiAlCl₄/SOCl₂ and (2.3M AlCl₃ + 0.5M LiAlCl₄)/SOCl₂ Electrolytes

	Storage Period (Months)											
Catalyst	Neutral Electrolyte				Neutral Electrolyte + 321 S.S.				Neutral Electrolyte + 316L S.S.			
	1	4	7	12	1	4	7	12	1	4	7	12
Without	(-)	(-)	(-)	(-)	4 (*) (71°C)	4 (*) (71°C)	4 (*) (71°C)	4 (71°C)	4 (*) (71°C)	4 (*) (71°C)	4 (*) (71°C)	4 (71°C)
With	4	4	4	4	4 (32°C)	4 (32°C)	4 (32°C)	4 (32°C)	4 (32°C)	4 (32°C)	4 (32°C)	4 (32°C)

Notes

- Stainless steel specimens were stored in sealed glass ampuls.

- Baseline analyses (Time = 0) were conducted on stainless steel samples, electrolyte, and electrolyte + (CoPc)ₙ.

- (*) Repeated for (0.5M LiAlCl₄ + 2.3M AlCl₃)·SOCl₂ acidic electrolyte.

- (-) These data base are available under a sponsored contract (ARRADCOM).

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composition and thus physically separated from the electrolyte during storage, the catalyst experiences operating temperature conditions only at 32°C (max).

The thionyl chloride from Moday Chemicals was distilled once before electrolyte preparation. The 1.5M $LiAlCl_4 \cdot SOCl_2$ solution was made by adding 1.5 moles of dried LiCl (Fisher Chemicals) and 1.5M $AlCl_3$ (Fluka Grade) to the distilled $SOCl_2$ in a 1 liter flask. The acidic electrolyte was made by adding 0.5 mole of LiCl and 2.8 moles of $AlCl_3$. Both electrolytes were mechanically stirred for 1-2 hours. Each ampul contained 10 ml of electrolyte.

The 316L and 321 stainless steels tested in these studies were sheared into strips 0.2" wide and 2" long. The 316L stainless steel was 0.005" thick; the 321 stainless steel was 0.025". Only half of the length of these specimens was immersed in the electrolyte and the other half remained above the electrolyte in a sealed ampul.

In preparation for storage, the stainless steel strips were washed in a hot (70°C) solution of 170 g Pennwalt Alkaline Detergent #36 cleaner in 1500 ml H_2O, heated in this solution for 5 minutes, and then rinsed with water. After rinsing, they were placed for 10 minutes in a 45°C pickling solution containing 20% by weight of water, followed by another rinsing in two successive H_2O baths. After the double rinsing, the strips were placed for 30 minutes in a hot (55°C) passivation solution made by slowly adding first 500 ml of conc. HNO_3 and then 56.2 g $Na_2Cr_2O_7$ to 2 liters of water, after which they were washed again in two successive H_2O baths. The strips were then dried of their excess water with paper towels and vacuum dried at 110°C overnight.

The $(CoPc)_n$ catalyst was synthesized and washed with 5% HCl to remove uncomplexed cobalt ions. It was then heat treated at 550°C for two hours in an inert atmosphere. After cooling to ambient temperature, 0.11 g was added to each storage ampul.

EVALUATION OF ELECTROLYTE AND STAINLESS STEEL SPECIMENS

Four ampuls from each group were taken out of storage for cobalt and iron analysis after each period. The ampuls containing stainless steel, both with and without

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catalyst, had undergone some yellow discoloration, more intense with the
acidic electrolytes than with neutral electrolytes. The intensity of
discoloration increased with storage time. After breaking the ampuls, the
electrolyte was vacuum filtered, and 12 ml of distilled water was added to
decompose $SOCl_2$.

- ## Electrolyte

To determine the presence of cobalt, a few drops of 1, 10-phenanthroline in
50:50 methanol-water (1% by weight) was added to the aqueous solution. A
light blue color would indicate the presence of cobalt ions, but none of the
ampuls tested so indicated - showing the catalyst to be stable for 12-month
storage.

Quantitative determination of Fe was done (using U.V. absorption technique)
on all groups of ampuls by pipetting 5 ml of electrolyte solution into a 100 ml
flask, adding 15-20 ml of water, and allowing the mixture to cool. The following
reagents, in the order listed, were added:

- a) 30 ml of a 50:50 (by volume) mixture of methyl ethyl ketone
     and methanol
- b) 5 ml of a 30% by weight NH_4SCN solution
- c) 5 ml of a 10% by weight $(NH_4)_2S_2O_4$ solution
- d) 10 ml of 1:1 HCl solution
- e) Dilute to mark with deionized water and mix well

A blank containing all reagents, except the electrolyte solution, was also made.

The presence of iron in these solutions gave an orange coloring. The absorbance
of each versus the blank was measured at 475 nm using the Bausch and Lomb
Spectronic 20. The concentrations in each solution are given in Table 3, as
based on a single absorption experiment.

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Table 3.   Iron Concentration in the Electrolyte After Storage

Group	Fe Concentration, μg/ml of Electrolyte			
	1 Month	4 Months	7 Months	12 Months
A	8.65	8.70	21.65	9.93
B	3.02	4.56	2.65	2.84
C	2.65	3.08	2.84	3.15
D	3.80	4.69	13.32	8.08
E	2.22	3.08	5.42	5.30
F	14.25	13.01	20.10	21.03
G	7.90	12.00	21.03	17.0
1.5M LiAlCl$_4$/SOCl$_2$	1.60	-	-	-
(2.3M AlCl$_3$ + 0.5M LiAlCl$_4$)/SOCl$_2$	0.37	-	-	-

Examination of Table 3 reveals that the iron concentration in the electrolyte in Groups B to E remains unchanged whereas in Groups F and G it increases slightly. The source of iron in ampul A was identified to be the stainless steel container used to heat treat the $(CoPc)_n$ catalyst at $550^{\circ}C$. Therefore, the higher values found in Groups F and G are the sum of the contamination in Groups A and B, and A and C, respectively. Since the stainless steel specimen did not contribute Fe contamination on storage in thionyl chloride electrolyte, experiments were not repeated with a Fe free $(CoPc)_n$ catalyst.

- ### Stainless Steel Specimens

The stainless steel specimens were separated from the electrolyte after reaching their storage periods noted in Table 2. The samples were washed with pure $SOCl_2$ and the excess solvent was removed with soft paper towels and dried under vacuum for several days (at least 7 days).

The specimens immersed in the neutral electrolyte showed no visible signs of corrosion, however, both the 316L and 321 strips stored in the acidic electrolyte showed light brown discoloration of their surface that were not immersed in the electrolyte. The surface and microstructural integrity of the electrolyte immersed and non-immersed portions of all stored specimens were subjected to both SEM and metallographic analysis.

SEM photomicrographs of stainless steel surfaces, fresh and after 4- and 12-month storage at $71^{\circ}C$, are shown in Figures 12-32. The photomicrographs show that 316L and 321 stainless steel surfaces were corroded in both the neutral and acidic electrolytes. The acidic electrolyte attacked the surface much more severely than neutral electrolyte. The surface corrosion appeared to slow down with storage time by the corrosion film. The part of the specimen that was not immersed, but exposed to electrolyte vapor, also exhibited surface corrosion similar to the part immersed directly in the electrolyte.

In order to evaluate the depth of the corrosion film, the cross sections of the specimens were examined by optical metallographis technique.

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DEVICE/PART NUMBER
Li/SOCl$_2$ Safety Studies

100X   200X   500X
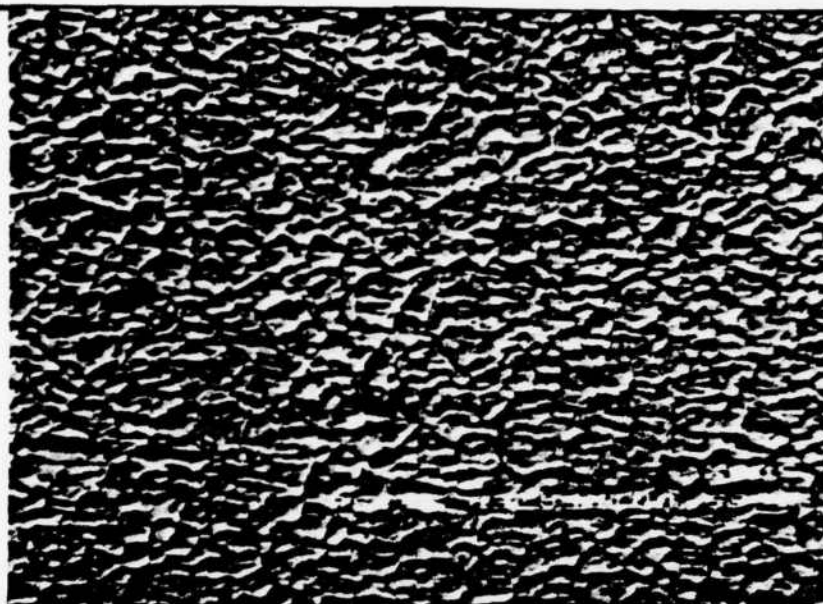
FIGURE	METALLURGICAL LABORATORY LOG NUMBER	COGNIZANCE
12	6669	J. Kasell - N Doddapaneni

Electron micrographs of the 321 stainless steel without exposure to Li/SOCl$_2$.

HP-532A

27

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DEVICE/PART NUMBER
Li/SOCl$_2$ Safety Studies

100X   200X   500X

FIGURE	METALLURGICAL LABORATORY LOG NUMBER	COGNIZANCE
13	6669	J. Kasell - N. Doddapaneni

Electron micrographs of the 316L stainless steel without exposure to Li/SOCl$_2$.

HP-532A

Honeywell
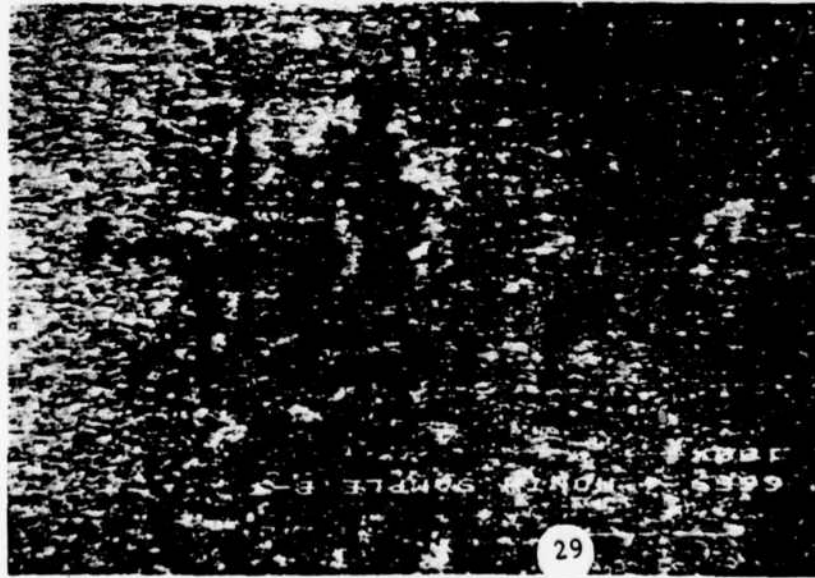
DEFENSE SYSTEMS DIVISION
600 SECOND STREET NE
HOPKINS, MN 55343

100X   200X   500X
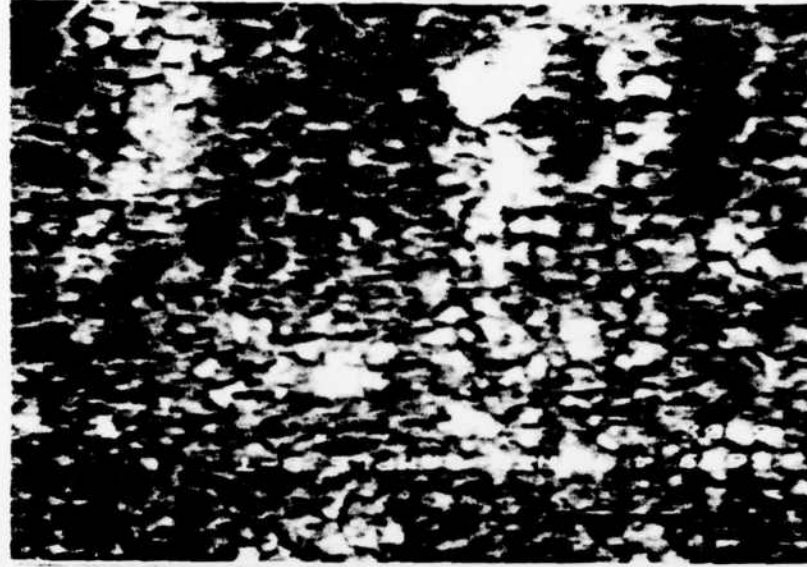
Electron micrographs of sample B Top after a four month exposure to Li/SOCl$_2$.

29

HP-532A

Honeywell

DEVICE/PART NUMBER

Li/SOCl₂ Safety Studies

100X   200X   500X .

FIGURE 15

METALLURGICAL LABORATORY LOG NUMBER 6669

COGNIZANCE J. Kasell - N. Doddapeneni

Electron micrographs of sample B bottom after a four month exposure to Li/SOCl₂.

30

HP-522A

Honeywell

DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies

500X

200X

100X

FIGURE	METALLURGICAL LABORATORY LOG NUMBER	COGNIZANCE
16	6669	J. Kasell - N. Doddapaneni

Electron micrographs of sample C bottom after four months exposure to Li/SOCl$_2$.

HP-532A

DEFENSE SYSTEMS DIVISION
600 SECOND STREET NE
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DEVICE/PART NUMBER
Li/SOCl$_2$ Safety Studies

100X   200X   500X

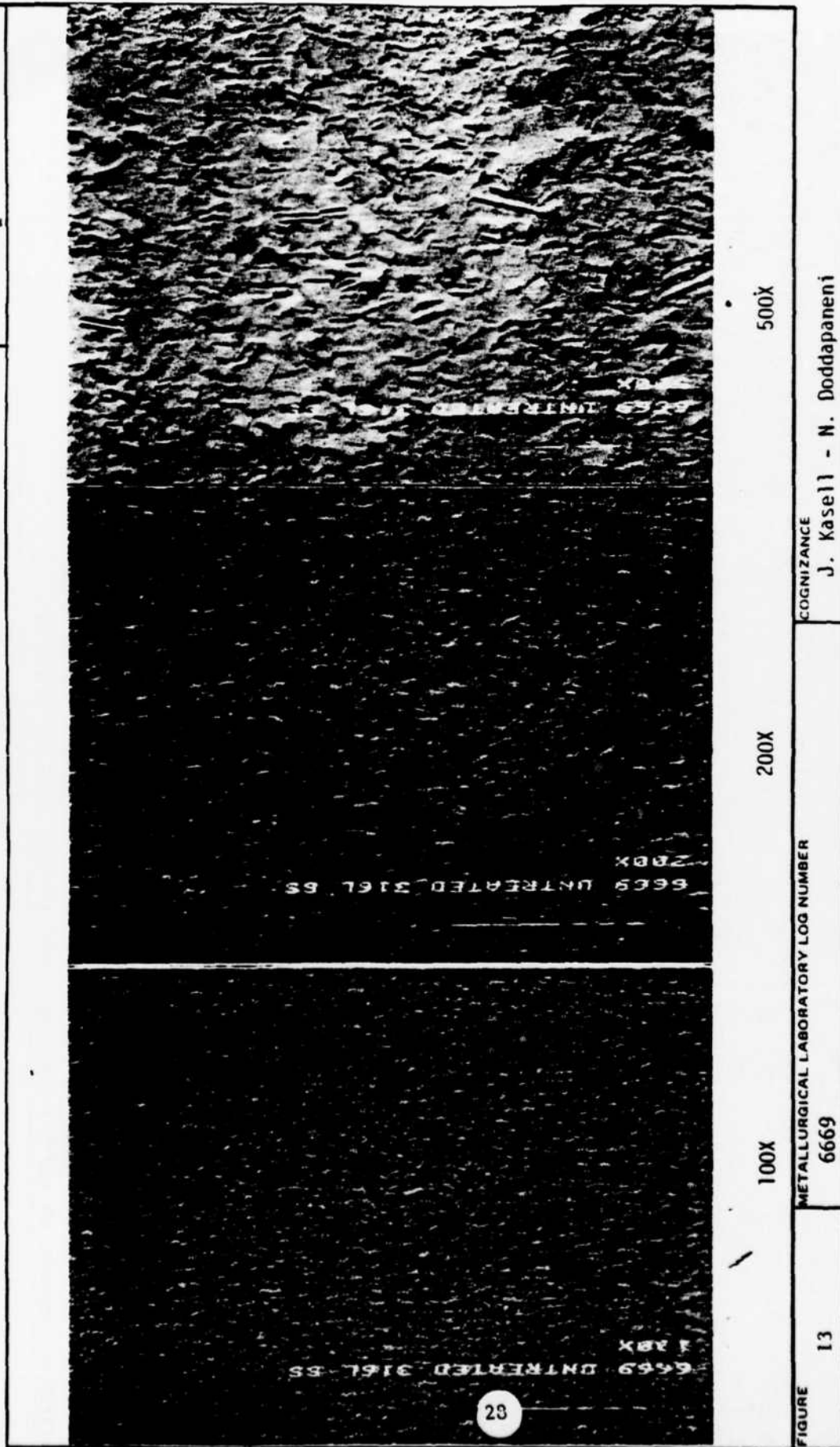| FIGURE 17	METALLURGICAL LABORATORY LOG NUMBER 6669	COGNIZANCE J. Kasell - N. Doddapaneni

Electron micrographs of sample D bottom after four months exposure to Li/SOCl$_2$.

HA 532A

Honeywell

100X

200X

500X

FIGURE	M&PE LOG NUMBER	COGNIZANCE	FTR NUMBER
18	6669	J. Kasell - N. Doddapaneni	

Electron micrographs of sample E bottom after a four month exposure to Li/SOCl$_2$.

HP 532A REV 9/75

Honeywell

DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies

100X   200X   500X
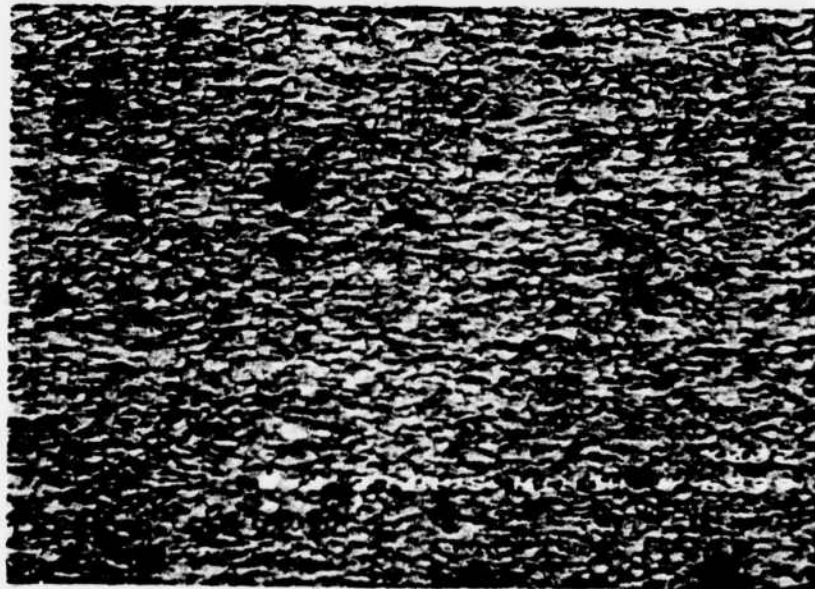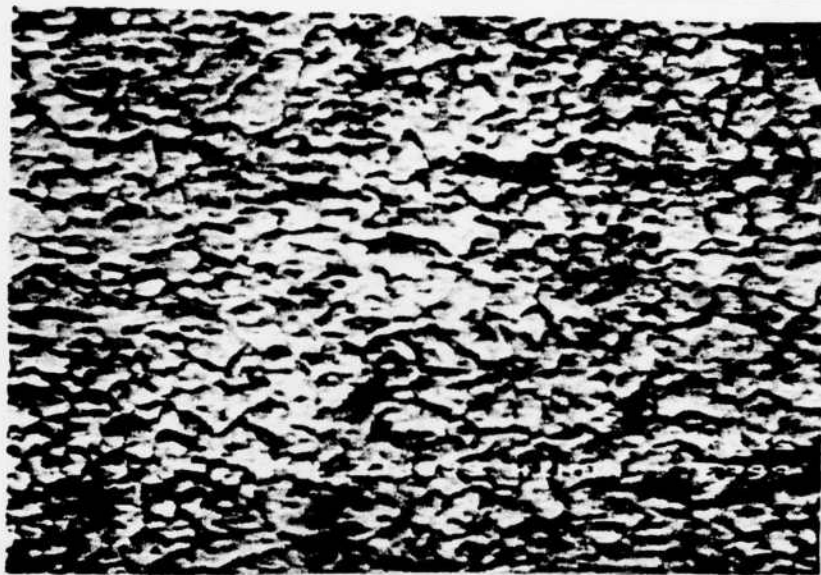
FIGURE	M&PE LOG NUMBER	COGNIZANCE	FTR NUMBER
19	6669	J. Kasell - N. Doddapaneni	

Electron micrographs of sample F bottom after four months exposure to Li/SOCl$_2$.

Honeywell

DEFENSE SYSTEMS DIVISION
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HOPKINS, MN 55343

DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies
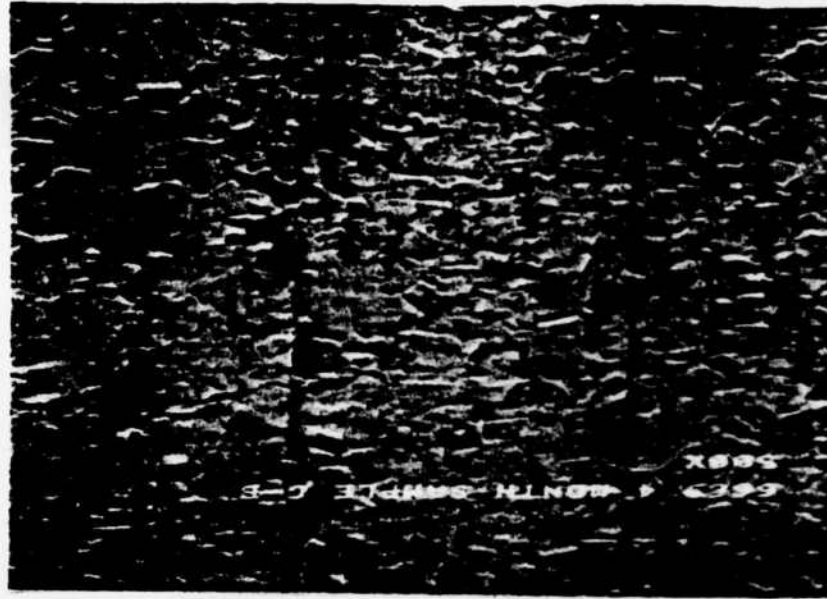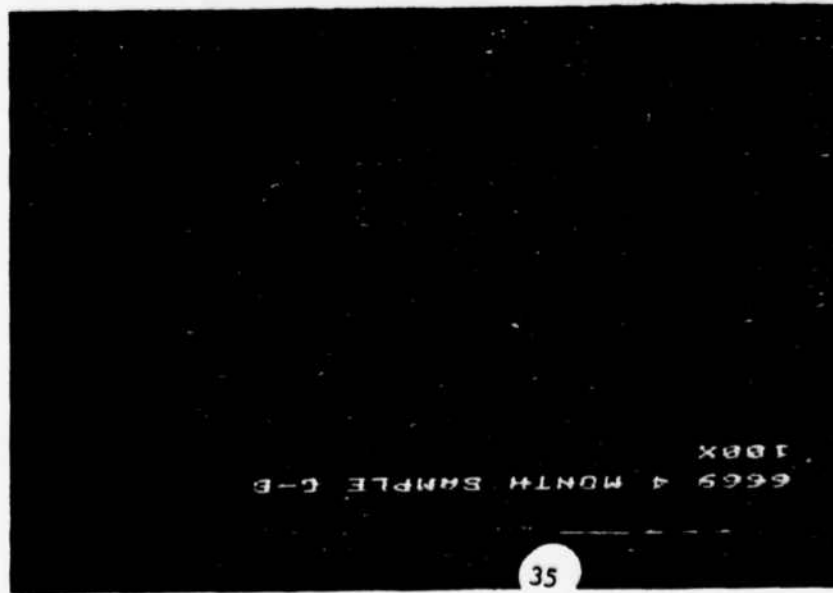
100X   200X   500X

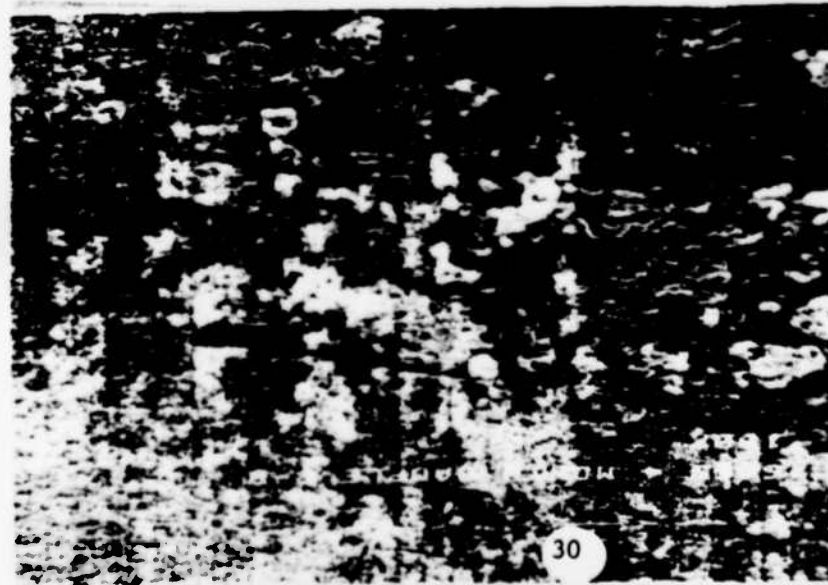| FIGURE	M&PE LOG NUMBER	COGNIZANCE	FTR NUMBER
20	6669	J. Kasell - N. Doddapaneni	

Electron micrographs of sample G bottom after four months exposure to Li/SOCl$_2$.

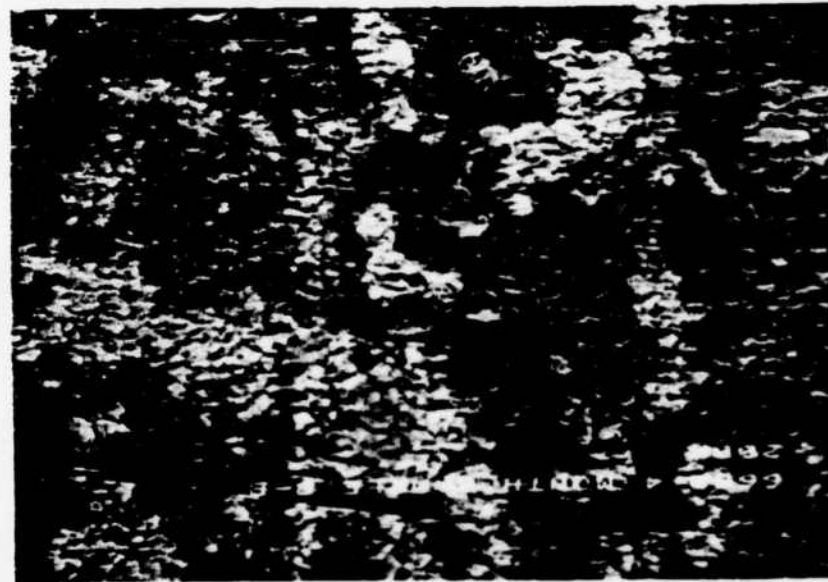DEFENSE SYSTEMS DIVISION
600 SECOND STREET NE
HOPKINS, MN 55343

DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies
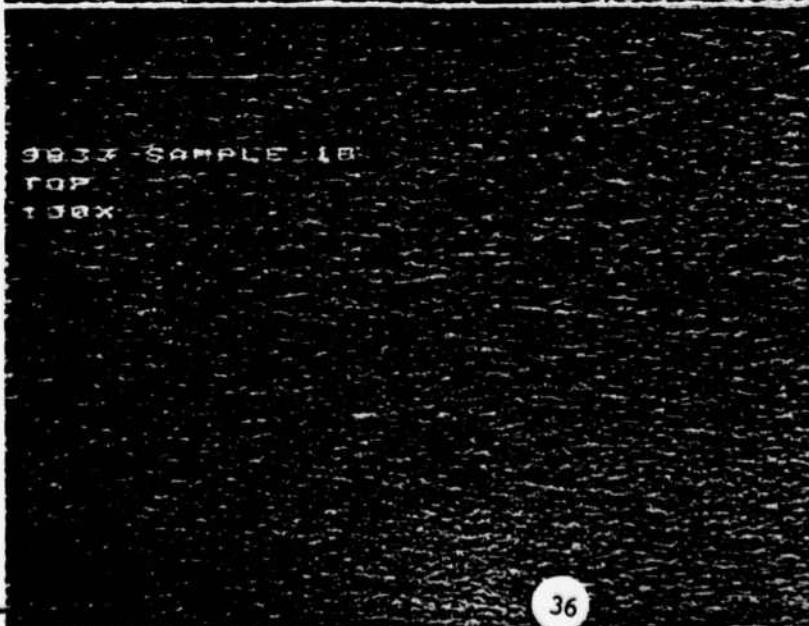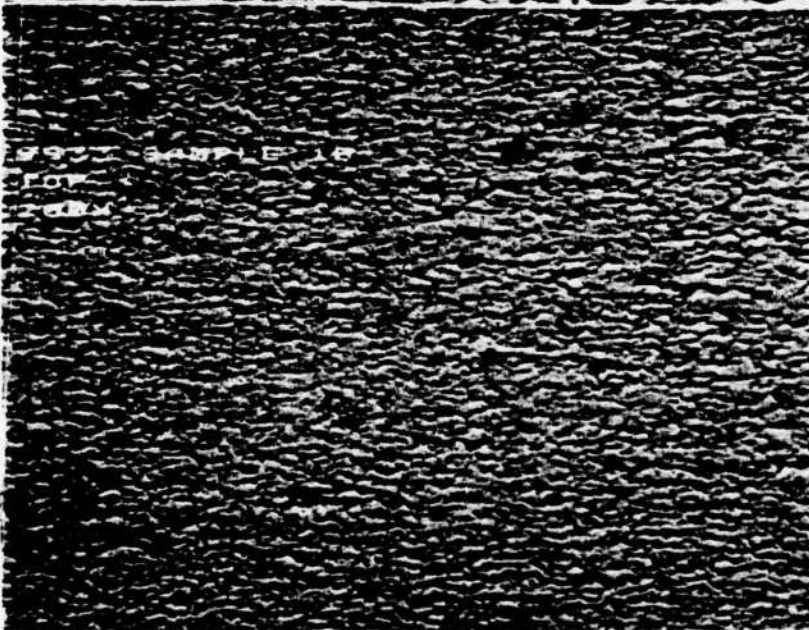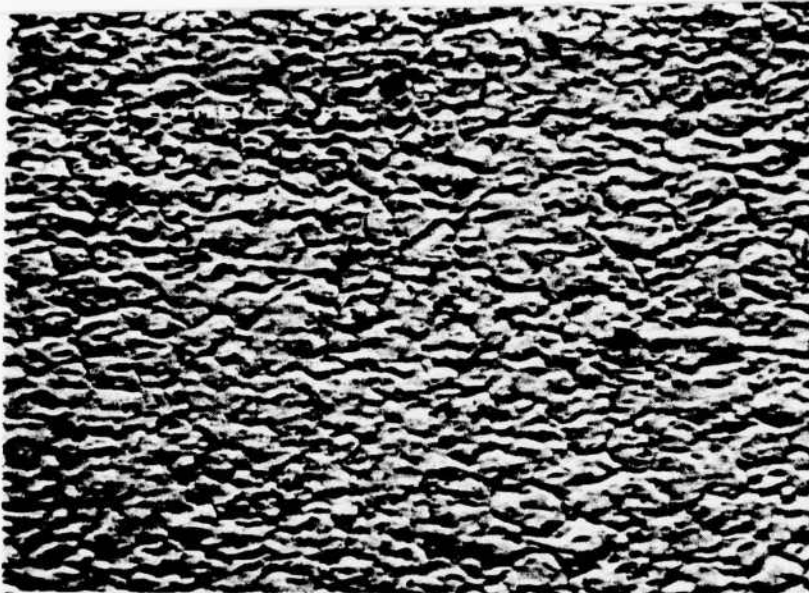
FIGURE	M&PE LOG NUMBER	ENGINEER	LTR NUMBER
21	9833	B. Schrupp/N. Doddapaneni	

Electron micrographs of sample 1B (top) after twelve months exposure to Li/SOCl$_2$

100X   500X

HP 532A REV 5/78

DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies
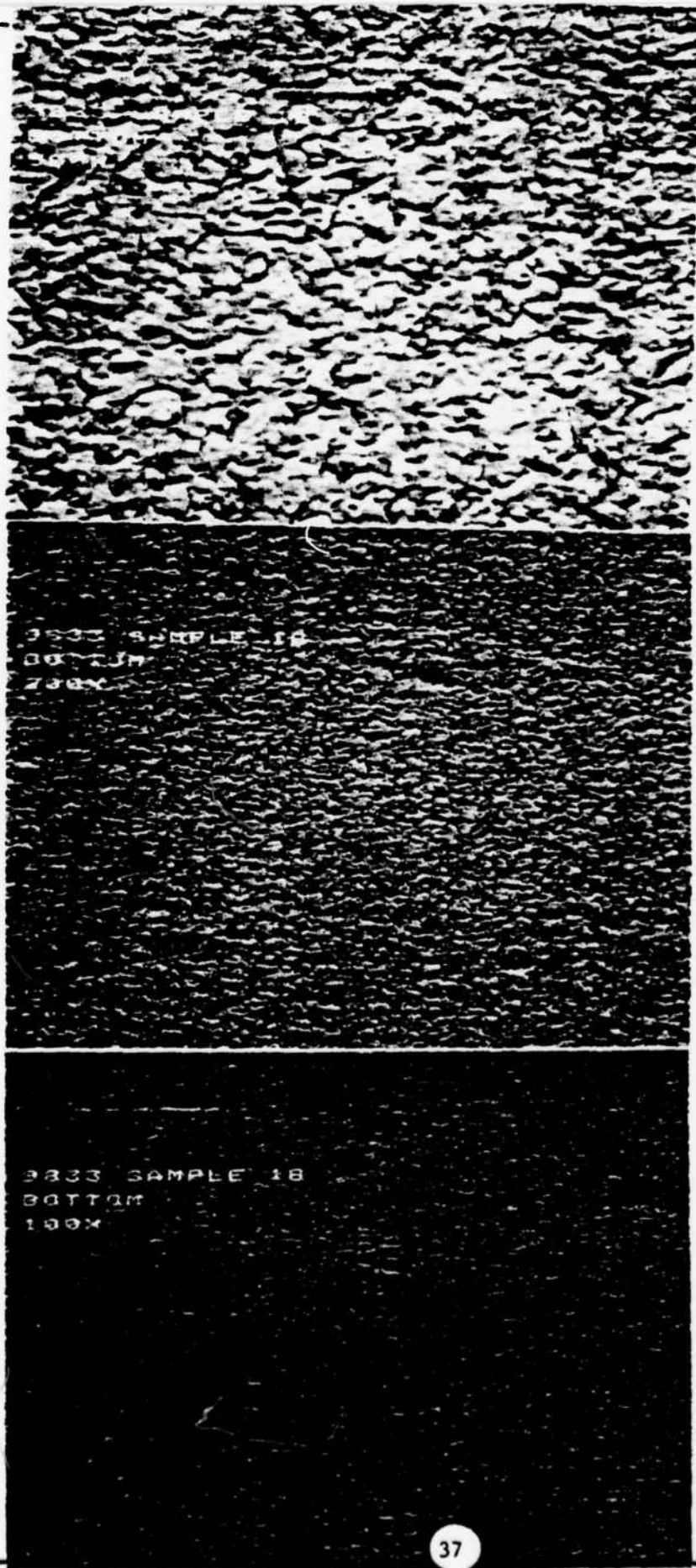
FIGURE			
22	9833		

B. Schrupp, N. Doddapaneni

Electron micrographs of smaple 1B (bottom) after twelve months exposure to Li/SOCl$_2$.

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DEVICE/PART NUMBER

L1/SOCl$_2$ Safety Studies

500X

200X

100X

COGNIZANCE

B. Schrupp/N. Doddapaneni
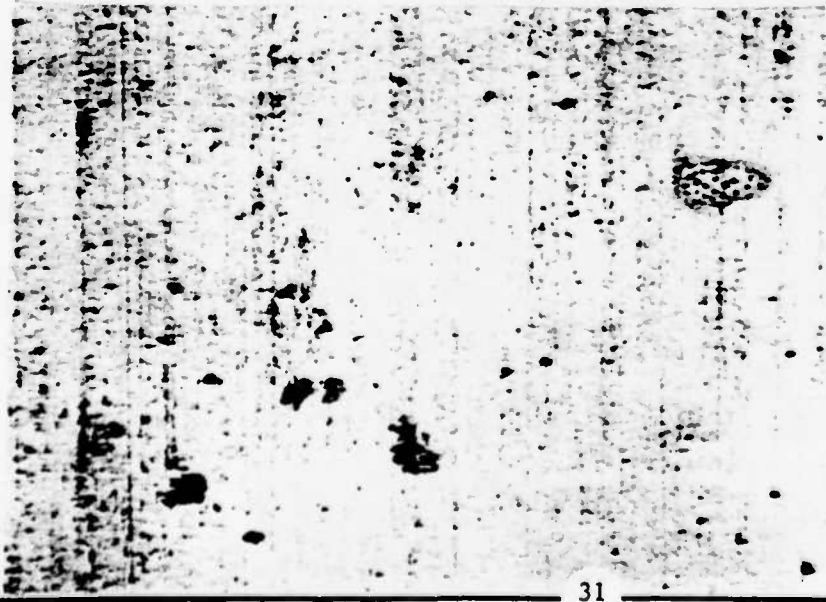
M&PE LOG NUMBER

9833

FIGURE

23

Electron micrographs of sample IC (top) after twelve months exposure to Li/SOCl$_2$.

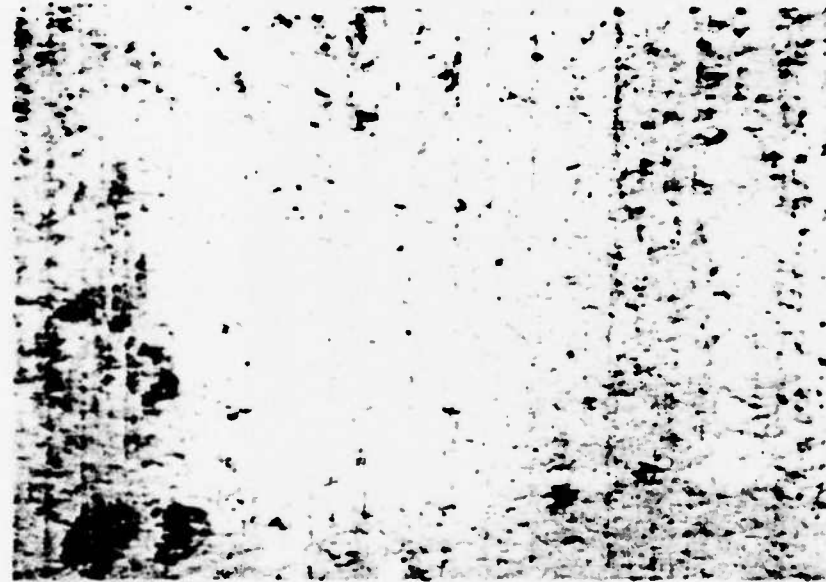DEFENSE SYSTEMS DIVISION
600 SECOND STREET NE
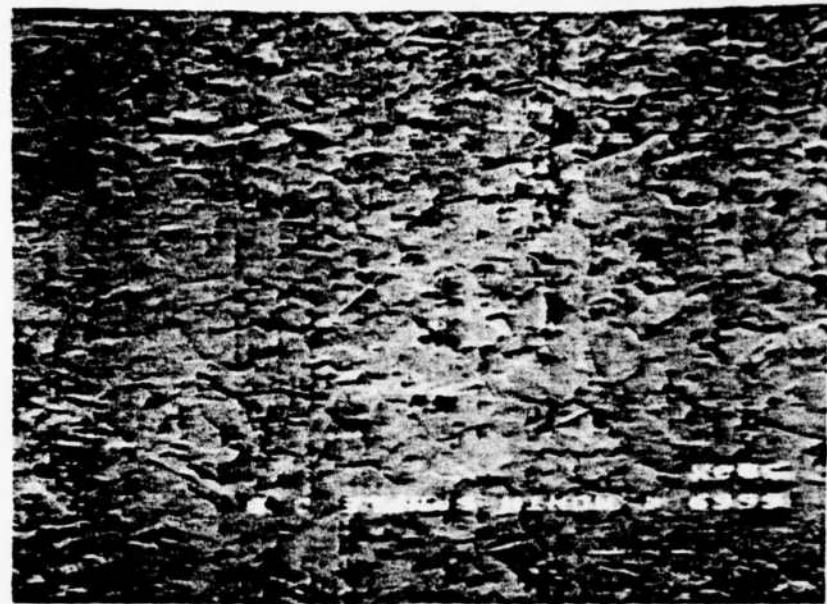HOPKINS, MN 55343

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DEVICE/PART NUMBER
Li/SOCl$_2$ Safety Studies

FIGURE	MLPE LOG NUMBER	COGNIZANCE	FTR NUMBER
24	9833	B. Schrupp/N. Doddapaneni	

Electron micrographs of sample 1C (bottom) after twelve months exposure to Li/SOCl$_2$.

100X 200X 500X

SAMPLE 1C
BOTTOM
100X

39

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DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies

100X   200X   500X

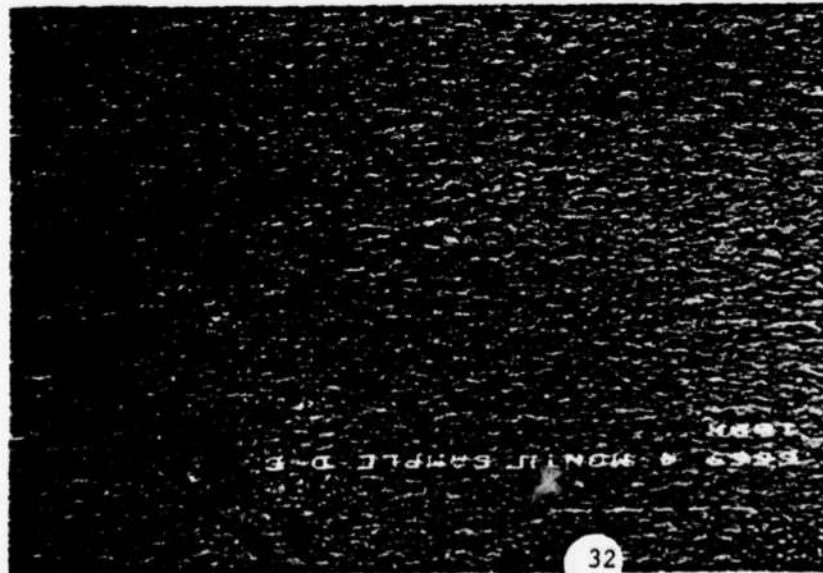| FIGURE	MFR. DOC. NUMBER	ITEM NUMBER
25	9833	B. Schrupp/N. Doddapaneni

Electron micrographs of sample 1D (top) after twelve months exposure to Li/SOCl$_2$.

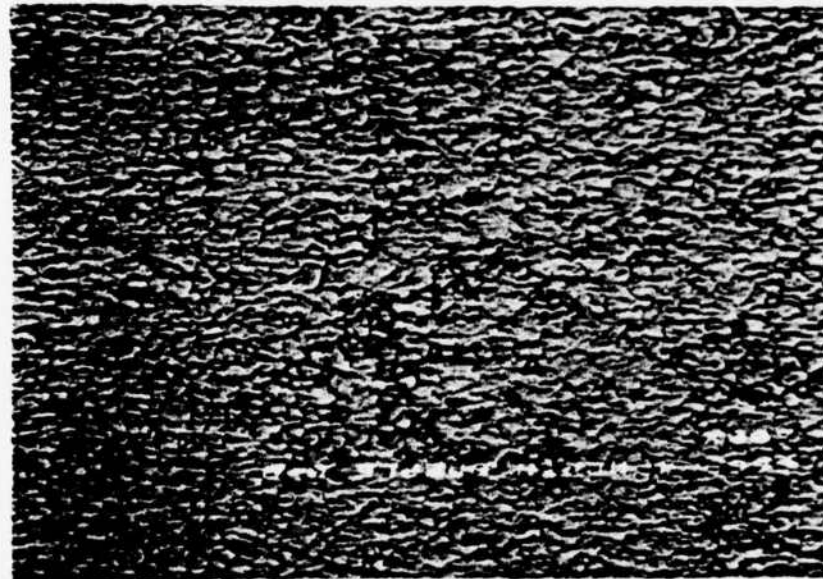DEFENSE SYSTEMS DIVISION
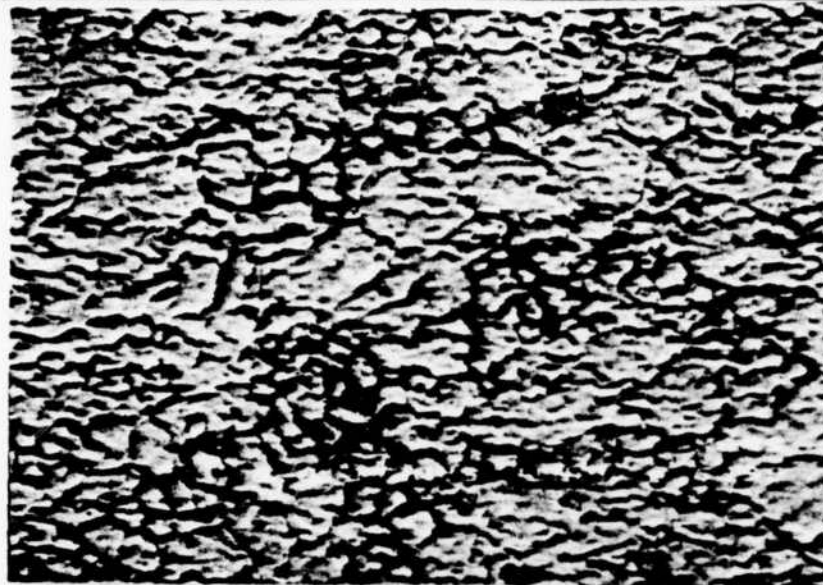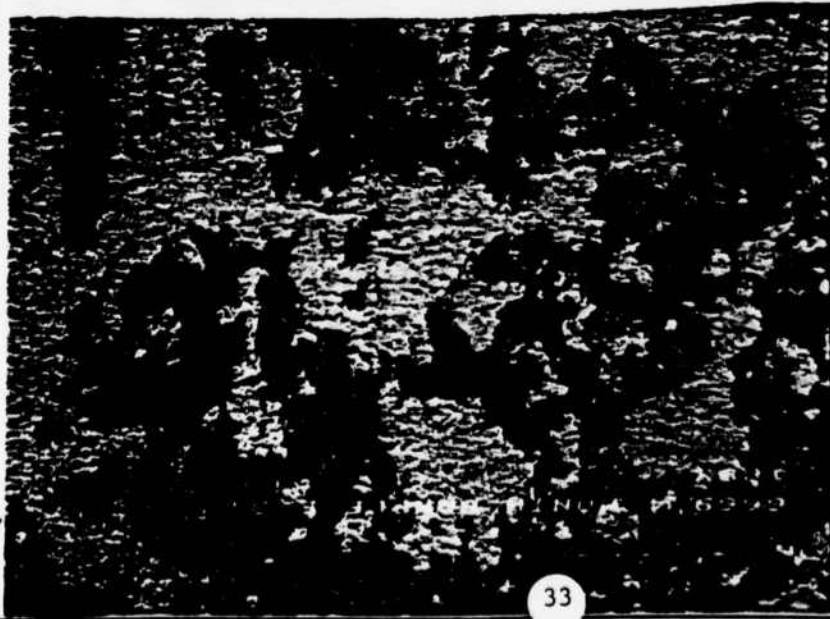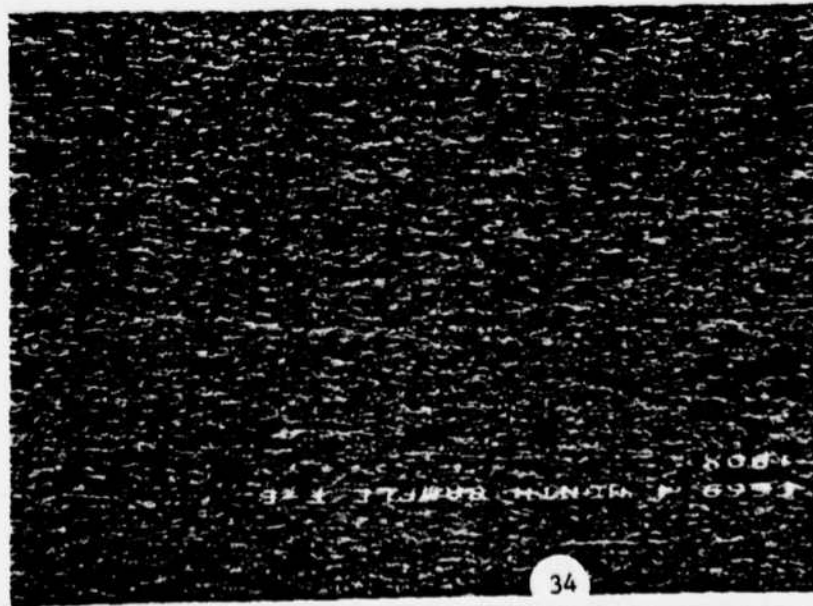600 SECOND STREET NE
HOPKINS, MN 55343

DEVICE/PART NUMBER
Li/SOCl$_2$ Safety Studies
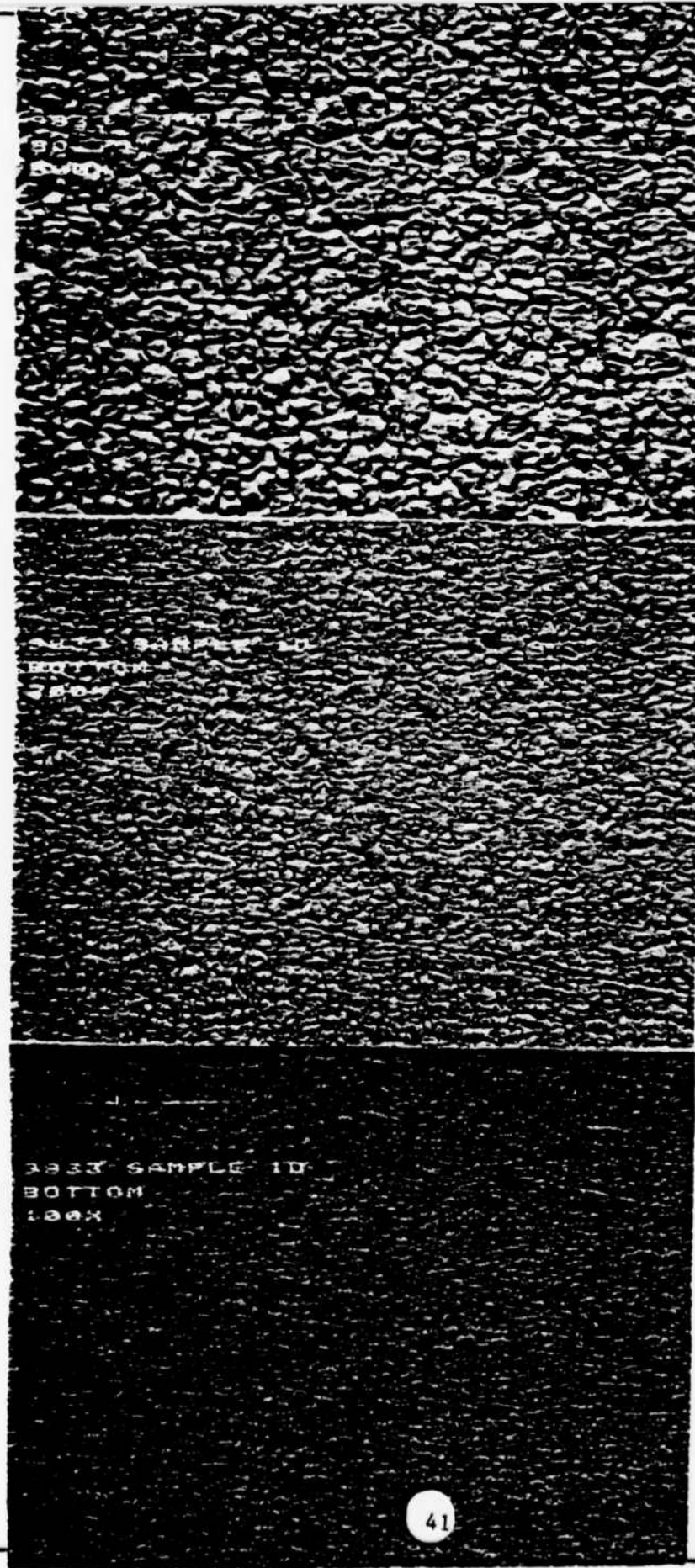
M&PF LOG NUMBER
9833

COGNIZANCE
B. Schrupp/N. Doddapaneni

FIGURE
26

Electron micrographs of sample 1D (bottom) after twelve months exposure to Li/SOCl$_2$.

100X   200X   500X

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DEVICE/PART NUMBER
L1/SOCl$_2$ Safety Studies

9833 SAMPLE 1E
TOP
500X

9833 SAMPLE 1E
TOP
200X

9833 SAMPLE 1E
TOP
100X

100X

200X

500X

FIGURE	M&PE LOG NUMBER	COGNIZANCE	FTR NUMBER
27	9833	B. Schrupp/N. Doddapaneni	

Electron micrographs of sample 1E (top) after twelve months exposure to L1/SOCl$_2$.

HP-532A REV 9/78

Elcetron micrographs of sample lE (bottom) after twelve months exposure to $Li/SOCl_2$.

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DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies

FIGURE	M&PE LOG NUMBER	COGNIZANCE		TECH NUMBER
29	9833	B. Schrupp/N. Doddapaneni		

Electron micrographs of sample 1F (top) after twelve months exposure to Li/SOCl$_2$.

100X   200X   500X

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DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies

100X   200X   500X

M&P LOG NUMBER

9833

B. Schrupp/N. Doddapaneni
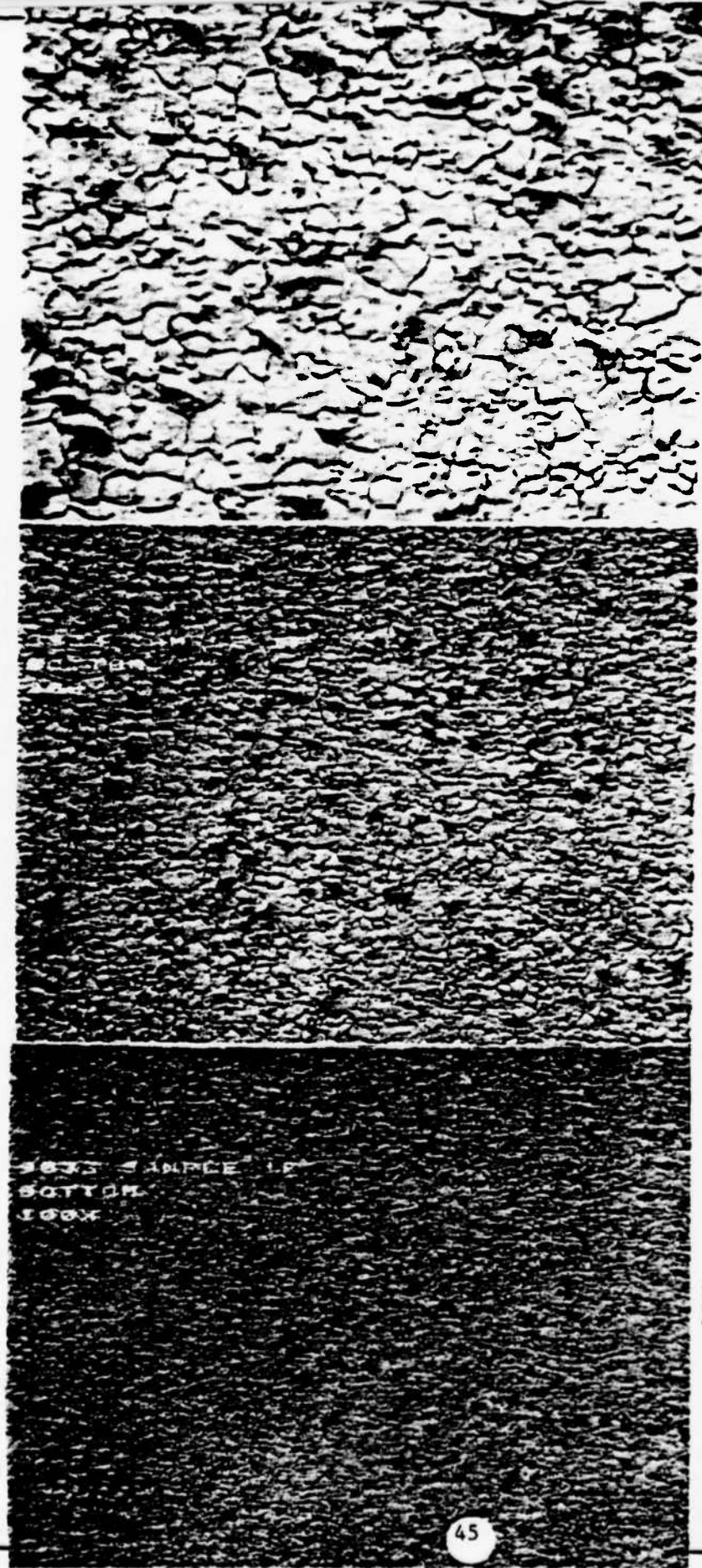
FIGURE 30

Electron micrographs of sample 1F (bottom) after twelve months exposure to Li/SOCl$_2$.

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DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Studies

100X   200X   500X

FIGURE	M&PE LOG NUMBER	COGNIZANCE	ETR NUMBER
31	9833	B. Schrupp/N. Doddapaneni	

Electron micrographs of sample 1G (top) after twelve months exposure to Li/SOCl$_2$.

46

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DEVICE/PART NUMBER
Li/SOCl₂ Safety Studies
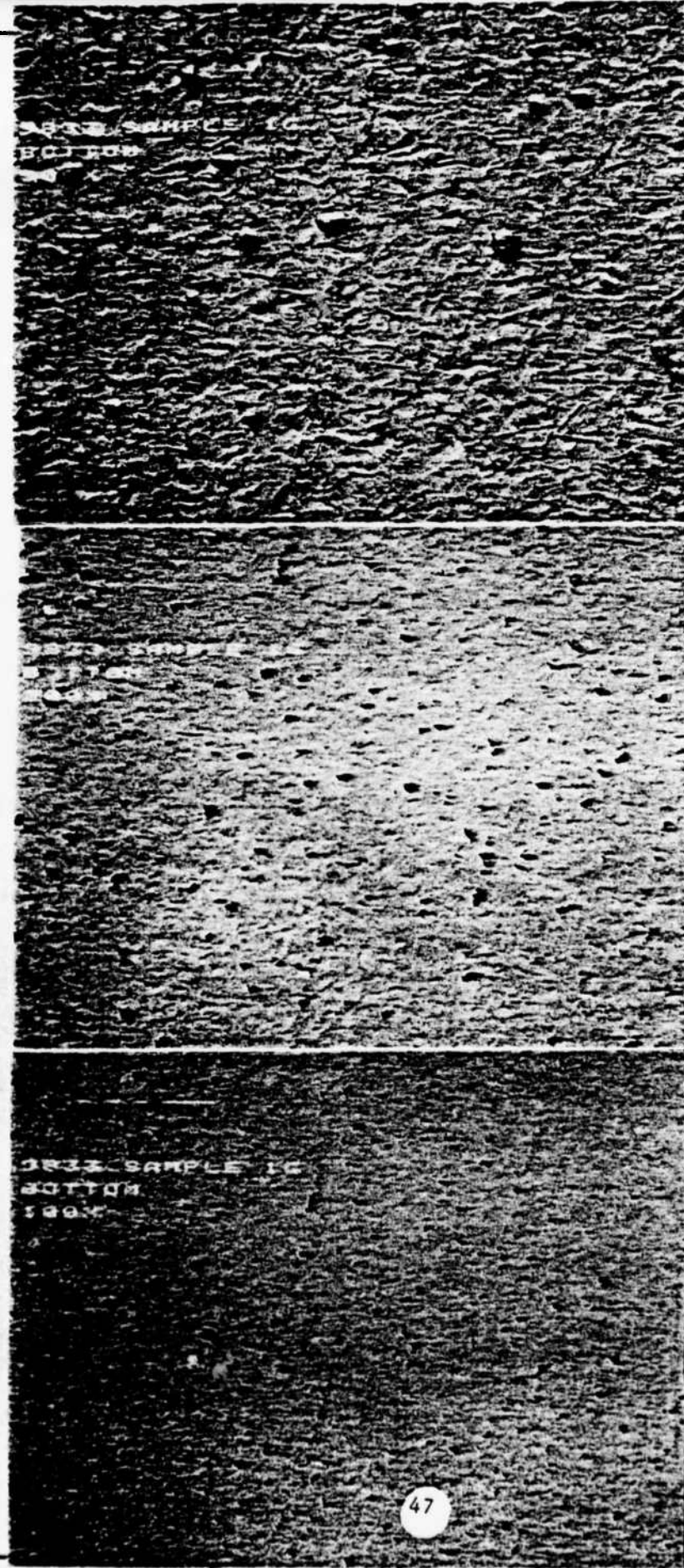
500X

200X

100X

FIGURE
32

M&PE LOG NUMBER
9833

COGNIZANCE
B. Schrupp/N. Doddapaneni

ETR NUMBER

Electron micrographs of sample 1G (bottom) after twelve months exposure to Li/SOCl₂.

HP 532A HF V 9/78

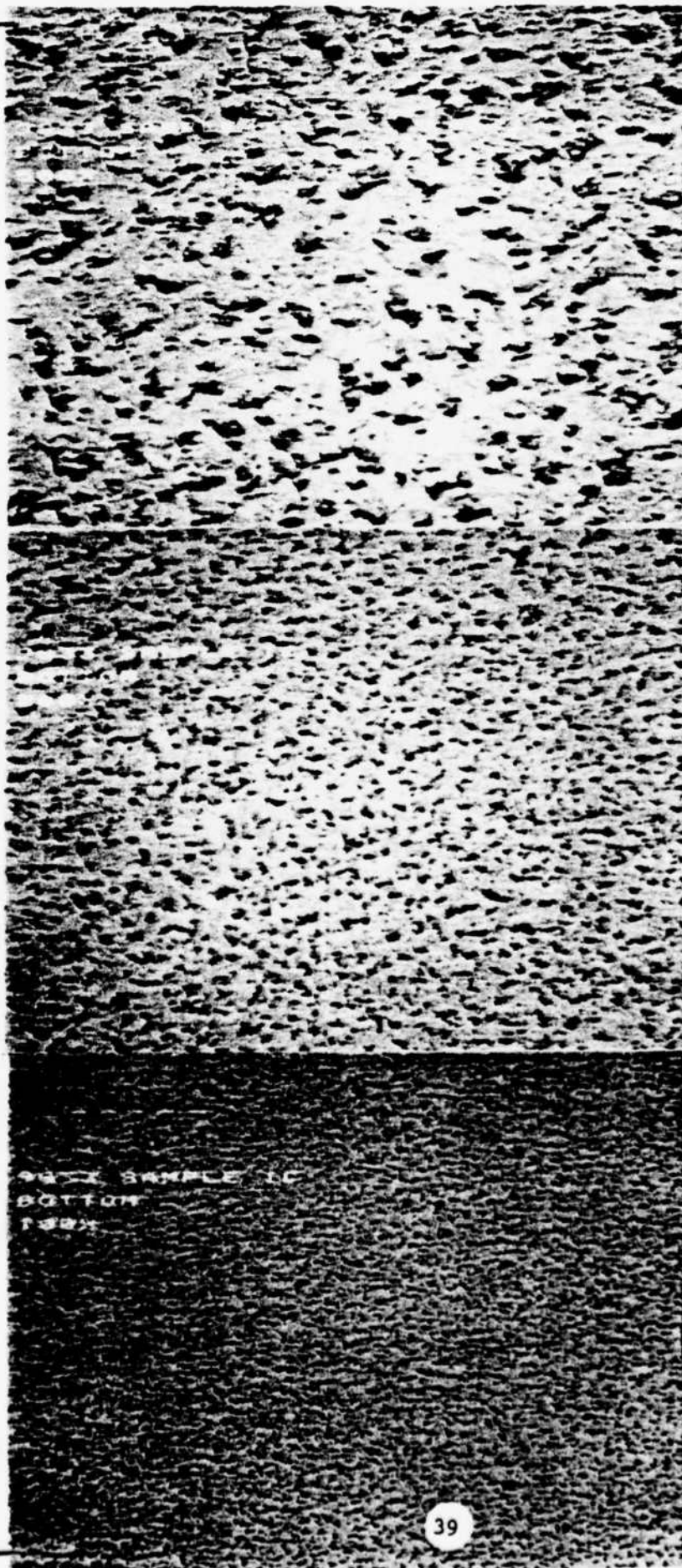The specimens were then cut and the edges were polished and etched before they were metallographically examined. Both the immersed and non-immersed (i.e., exposed to vapor phase) edges of the specimens were studied.

In Figure 33, the photomicrographs of the edges of fresh 321 and 316L stainless steel specimens are given. The optical metallographic studies of these specimens after exposure to both acidic and neutral electrolyte for 1, 4 and 7 months (12-month stored specimens were not analyzed by this technique) at $71^{\circ}C$ revealed no significant penetration of corrosion into the specimens. For example, the photomicrographs of specimens after 7-month exposure showed no significant difference from specimen-to-specimen (Figures 34 - 39). Based on this limited study, it can be concluded that the surface corrosion of both 316L and 321 stainless steel specimens takes place and that these surface films either eliminate or significantly reduce further corrosion in both acidic and neutral electrolyte. In addition, the presence of $(CoPc)_n$ catalyst does not appear to affect the surface corrosion.

In conclusion, we believe that both 316L stainless steel and 321 stainless steel can be used as materials of construction for the electrolyte reservoir in reserve batteries. In cell design that uses stainless steel as the positive collector grid, however, the influence of the surface film on cell polarization should be determined, especially in applications that require high intermittent pulses during a long operating mission life.

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DEVICE/PART NUMBER

L1/SOCl$_2$ Safety Studies

A

B

FIGURE	METALLURGICAL LABORATORY LOG NUMBER	COGNIZANCE
33	6669	D. Dehmer - D. Doddapaneni

Photomicrographs of both edges of the untreated 321 stainless steel (View A) and the untreated 316L stainless steel (View B).

Magnification: 575X.

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DEVICE/PART NUMBER
Li/SOCl$_2$ Safety Study

View A
Top

View B
Bottom

FIGURE	M&PE LOG NUMBER	COGNIZANCE	ETR NUMBER
34	8031	B. Nielson/N. Doddapaneni	

Photomicrographs of Sample B after a seven month exposure to Li/SOCl$_2$. Magnification: 575X.

50

DEVICE/PART NUMBER

Li/SOCl$_2$ Safety study

View B
Bottom

View A
Top

FTR NUMBER

FIGURE	M&PE LOG NUMBER	COGNIZANCE
35	8031	B. Nielson/N. Doddapaneni

Photomicrograph of Sample C after a seven month exposure to Li/SOCl$_2$. Magnification: 575X.

51

Honeywell

DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Study

View A
Top

View B
Bottom

FIGURE	M&PE LOG NUMBER	COGNIZANCE	ETR NUMBER
36	8031	B. Nielson/N. Doddapanent	

Photomicrograph of Sample D after a seven month exposure to Li/SOCl$_2$. Magnification: 575X.

52

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DEVICE/PART NUMBER

L1/SOCl$_2$ Safety Study

View B
Bottom

View A
Top

FIGURE	M&PE LOG NUMBER	COGNIZANCE	ETR NUMBER
37	8031	B. Nielson/N. Doddapaneni	

Photomicrograph of Sample E after a seven month exposure to L1/SOCl$_2$. Magnification: 575X.

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DEVICE/PART NUMBER

L1/SOCl$_2$ Safety Study

View A
Top

View B
Bottom

ETR NUMBER

FIGURE	M&PE LOG NUMBER	COGNIZANCE
38	8031	B. Nielson/N. Doddapanenl

Photomicrograph fo Sample F after a seven month exposure to L1/SOCl$_2$. Magnification: 575X.

54

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DEVICE/PART NUMBER

Li/SOCl$_2$ Safety Study
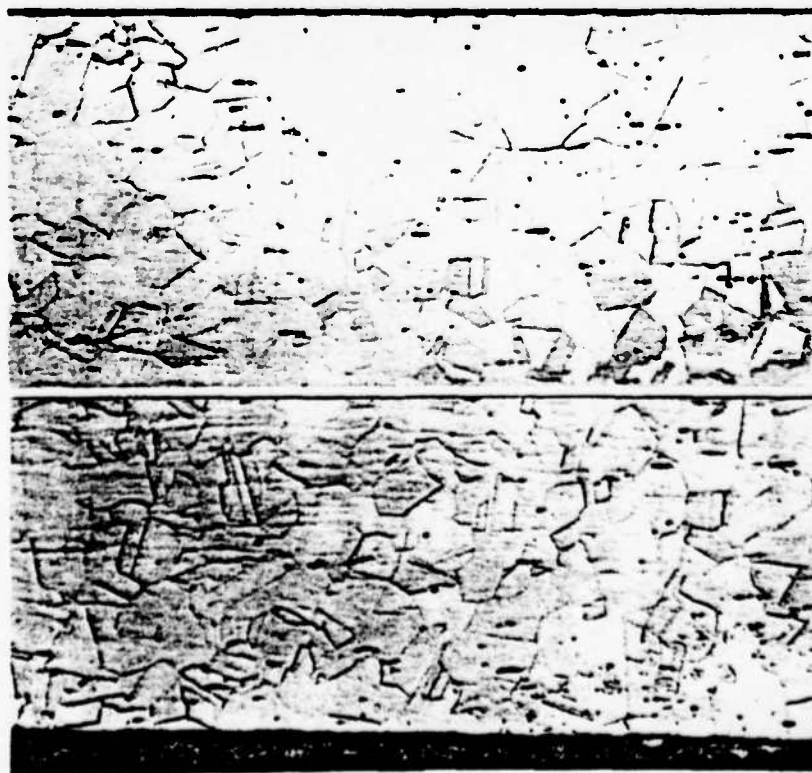
View A
Top
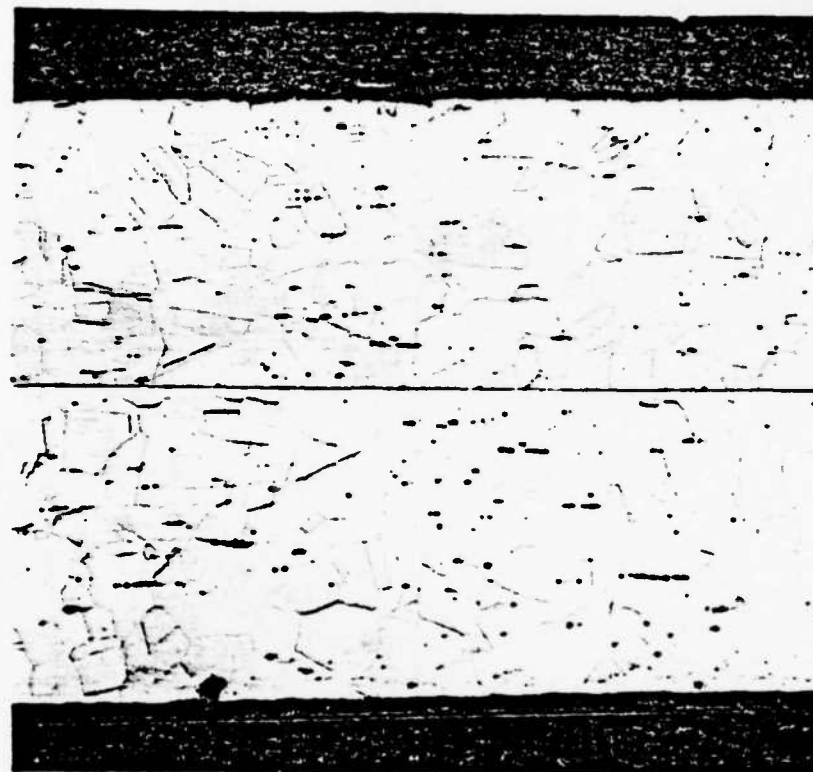
View B
Bottom

| FIGURE 39 | M&PE LOG NUMBER 8031 | COGNIZANCE B. Nielson/N. Doddapaneni | ETR NUMBER |

Photomicrograph of Sample G after a seven month exposure to Li/SOCl$_2$. Magnification: 575X.

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4.0 FORCED DISCHARGE INTO REVERSAL

One of the problems related to a multicell battery is that some of the
cells might go into reversal on load and create hazards. The extent of the
safety hazard depends on cell design, i.e., anode-limited or cathode-limited.
To evaluate the impact of cell design features on safety, spirally wound cells
(Figure 40) were built and tested at various discharge and forced overdischarge
current densities. Each cell was equipped with a pressure transducer and a
valve for activation and for tapping gas samples. Twelve (12) cells were also
equipped with internal thermocouples. The glass container was placed in a plastic
jacket for protection from flying glass pieces if an explosion was to occur.

There were six types of wrap cells studied:

- Anode-limited cell without catalyst
- Anode-limited cell with $(CoPc)_n$ catalyst
- Anode-limited cell with FePc catalyst
- Cathode-limited cell without catalyst
- Cathode-limited cell with $(CoPc)_n$ catalyst
- Cathode-limited cell with FePc catalyst

ANODE-LIMITED DESIGN

Anode-limited cells were built with two layers of 0.008" thick lithium foil.
Since it was felt that the concentration of LiCl in the discharged cell appears
to contribute to the cell behavior under reversal conditions, the cells were
built with 4.88 ± 0.42 Ah of theoretical lithium capacity instead of without
lithium on the current collector (316L stainless steel). The physical
characteristics of the anode-limited cell components were:

Anode   Dimensions:*   1.75" x 3.75" x (0.011 ± 0.001)"
         No. of Pieces: 2
         Anode Weight: 1.27 ± 0.11 g
         Anode Capacity: 4.88 ± 0.42 Ah
         * For cells 1, 2, 3   1.75" x 3.75" x 0.006"

                                     Anode Wt.   0.75 g ; Capacity 2.89 Ah

57
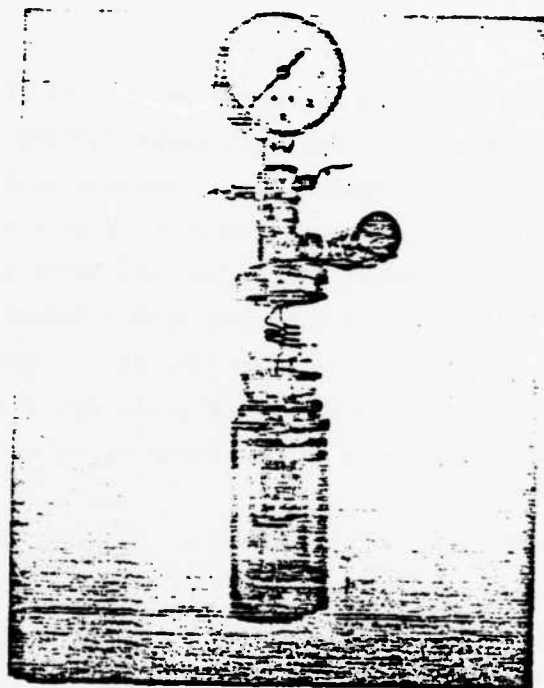
FIGURE 40.   LABORATORY CELL FIXTURE TO SIMULATE D-CELL TESTS

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Cathode	Dimensions:	1.75" x 3.6" x 0.010" for anode
Steel		1.75" x 3.9" x 0.010" for cathode
Grids		

Separators: Manning Non-Woven Glass Mat

                    Dimensions: 2" x 8.5" x 0.005"

                    No. of Pieces/Cell: 4

Electrolyte: 1.5M $LiAlCl_4/SOCl_2$

                    Amount 17 ml or 20 ml

Attachments: Pressure Transducer

                    Pressure Relief Valve

                    Volume: 3 ml

A total of 18 anode-limited cells were built. The effect of the quantity
of lithium and the quantity of electrolyte were tested for cell safety
during forced overdischarge into reversal. Cells 1-13 contained 20 ml of
electrolyte and cells 14-18 contained 17 ml of electrolyte. All cells were
discharged at a constant current of 1 mA/cm^2 (based on cathode area) with
diode protection. Each experimental setup consisted of 3 cells connected in a
series and discharged and forced overdischarged. The average voltage, discharge
time and the cell pressure at the end of 100% depth of discharge to 0.7 volts
are given in Table 4. Cells with catalyzed cathodes have higher voltages than
cells with baseline cathodes. Cells 12, 15 and 18 contained tetrasulphonated
iron phthalocyanine (TsFePc) catalyst. This catalyst is water soluble and
therefore can be impregnated easily and efficiently onto the carbon electrode.
In the case of the FePc catalyst, which was added to the electrolyte before
activation, severe voltage delays were encountered if the activated cells were
not subjected to discharge within ten minutes. With TsFePc impregnated cathodes,
the voltage delay effects were slightly minimized, however, the cell voltages
were lower with TsFePc than with the FePc catalsyt.

After discharge to 0.7 volts, the diodes were removed and cells were subjected
to forced overdischarge into reveral at various current densities. The cell
voltages and the pressures at the ends of the noted depths of discharge at their
corresponding current densities are given in Table 5. Cells 1-3, which contained

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Table 4. Discharge Performance of Anode-Limited Cells

Cell No.	Catalyst	Rate, mA/cm^2	Discharge Time to 2.0 V, (Hrs)	Avg. Cell Voltage (volts)	Pressure at 100% DOD, psig
1	-	1	20	3.40	10
2	$(CoPc)_n$	1	26	3.50	18
3	FePc	1	30	3.50	6
4	-	1	36	3.38	3 (leak)
5	$(CoPc)_n$	1	36	3.50	18
6	FePc	1	35	3.51	3
7	-	1	28	3.38	10
8	$(CoPc)_n$	1	28	3.48	18
9	FePc	1	28	3.51	3
10	-	1	21	3.39	11
11	$(CoPc)_n$	1	31	3.50	10
12	TsFePc	1	27	3.50	18
13	-	1	40	3.36	10
14	$(CoPc)_n$	1	49	3.51	16
15	TsFePc	1	46	3.52	18
16	-	1	35	3.39	10
17	$(CoPc)_n$	1	40	3.49	16
18	TsFePc	1	43	3.50	12

Note: Variation in the discharge time is due to variation in the anode thickness.

Table 5. Overdischarge of Anode-Limited Cells into Reversal

Cell No.	Catalyst	Overdischarge Rate (mA/cm²)	Cell Voltage, V	DOOD %	Pressure at the End of Overdischarge, psig
1	-	2	-1.2	70	12[1]
2	(CoPc)$_o$	2	2.4	30	18[1]
3	FePc	2	5.0	30	39[1]
4	-	5	-4.0	100	20
		10	-5.6	100	98
		20	-4.6	100	180
		30	-3.1	150	220
5	(CoPc)$_n$	5	-4.0	100	46
		10	-4.9	100	114
		20	-4.8	100	231
		30	-4.9	150	240
6	FePc	5	-4.4	100	22
		10	-5.4	100	48
		20	-4.1	100	177
		30	-4.2	150	195
7	-	5	-3.9	125	37
		10	-4.5	100	92
		15	-4.7	100	156
		20	-4.5	100	213
		30	-3.7	100	280
8	(CoPc)$_n$	5	-3.3	100	51
		10	-3.5	100	88
		15	-4.2	100	160
		20	-4.6	100	280
		30	-9.0	5	320[2]
9	FePc	5	-4.45	125	23
		10	-5.15	100	70
		15	-5.2	100	121
		20	-5.2	100	191
		30	-4.15	100	224
10	-	2	-1.23	53	12
11	(CoPc)$_o$	2	-5	53	19.2 } 3
12	TsFePc	2	-4.95	53	39.5
13	-	5	-5.5	100	71
		10	-5.6	100	130
		15	-6	100	180
		20	-4.7	100	195
		30	-4.2	100	236
14	(CoPc)$_o$	5	Cell failed after 1 hr.	8	>100
15	TsFePc	5	-5.5	100	35
		10	-5.5	Cell fixture shattered after 2 hrs. at 10 mA/cm², at a pressure of 134 psi.		
16	-	5	-5.1	100	72
		10	-6.4	67	150
17	(CoPc)$_o$	5	-4.6	100	70 } 4
		10	-6.6	67	136
18	TsFePc	5	-4.6	100	97
		10	-6.2	67	168

(1) Forced overdischarge into reversal was stopped before cells vented.
(2) Stopped because of continuous voltage drop.
(3) Test equipment failure forced to disbandon these cells before venting.
(4) Stopped after 10 mA/cm² forced overdischarge because of high cell pressure.

61

0.75 g of lithium, showed severe voltage drops during forced overdischarge even at 2 mA/cm^2. Therefore, they were discarded. The abnormal drop in voltage in these cells could be due to electrode stack pressure. Cells 4-18 , containing approximately 1.27 $\pm$ 0.11 g of lithium on the anode grid, also showed high voltage drops ranging from -4.0 to -7.0 volts.

Cells 14-18, which contained only 17 ml of electrolyte, also showed very high pressures and hence were discontinued. The cause of high pressure buildup could have been due to heat generation in the not-so-flooded cells. Cells 4-13, regardless of cathode type, sustained forced overdischarge current up to 30 mA/cm^2. During cell reversal, severe heat generation occurred and, therefore, very high pressures were recorded. However, in direct contrast to the cathode-limited cell design (see below under Cathode-Limited Design), the anode-limited design cells under flooded conditions did not vent even after 30 mA/cm^2 overdischarge currents. Typical discharge and forced overdischarge characteristics of anode-limited cells are given in Figures 41-46.

All cells were dismantled immediately after cell reversal. Temperatures of more than 100°C were measured in the open electrode stack in all cells. The actual temperature during cell reversal studies, therefore, could be much higher than 100°C as measured in the open electrode stacks.

CATHODE-LIMITED DESIGN

Cell reversal studies with cathode-limited design were conducted in order to assess the design impact on safety. Cells tested consisted of baseline cathode, (CoPc)$_n$ catalyzed cathodes and FePc catalyzed cathodes. Cathode-limited wrap cells were first discharged with diode protection and after removing diode, then forced overdischarged into reversal. Each experimental setup consisted of 3 cells connected in series during both discharge and reversed overdischarge. The physical characteristics of the cathode-limited cell components were:

Anode - Two pieces of lithium sandwiched on grid.

Dimensions:	1.75" x 3.75" x 0.020" (two pieces)
Weight:	2.35 g
Capacity:	2.35 x 3.86 = 9.07 Ah

62
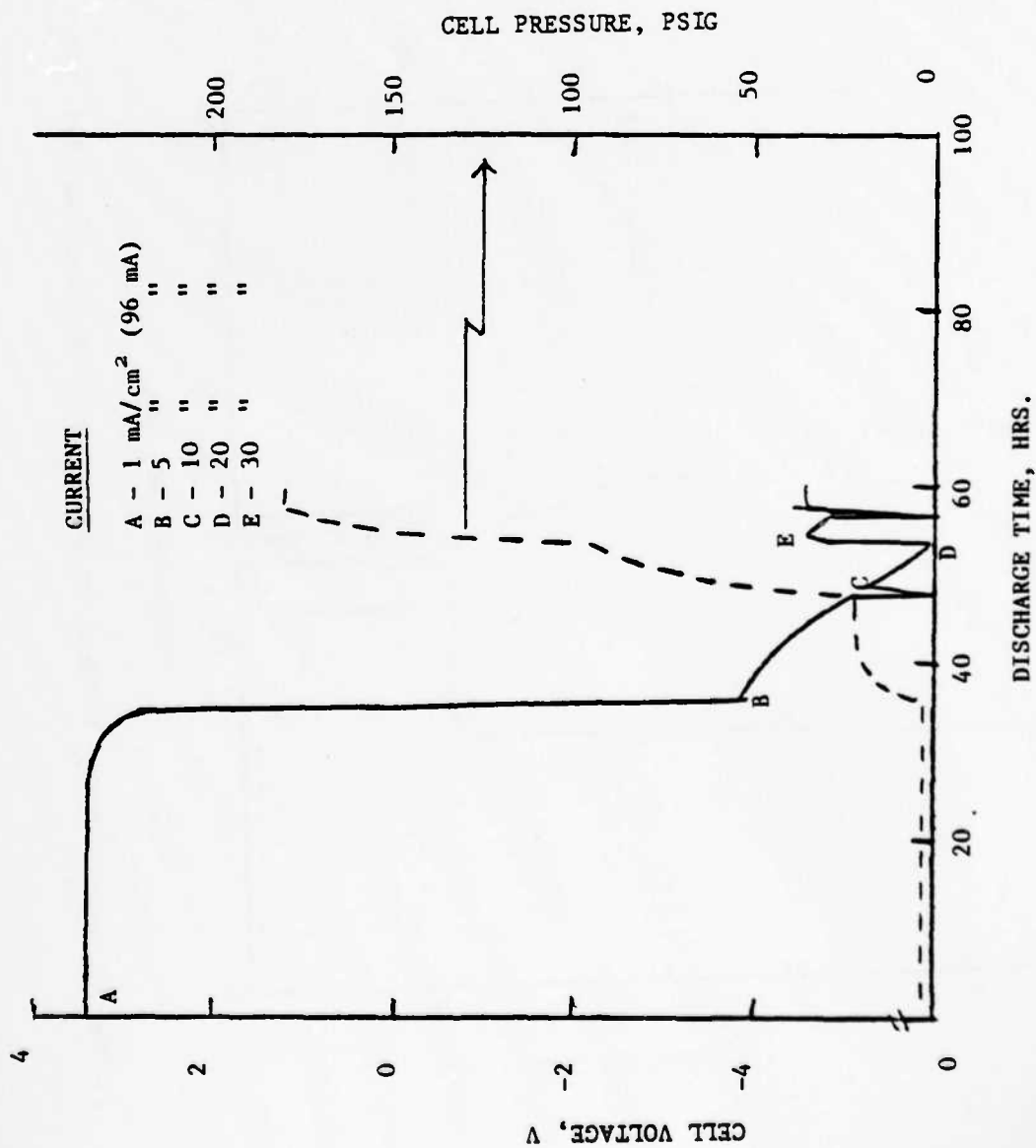
FIGURE 41. DISCHARGE AND REVERSAL OF A BASELINE, ANODE-LIMITED LAB WRAP CELL CONTAINING 1.25 g OF LITHIUM.

63
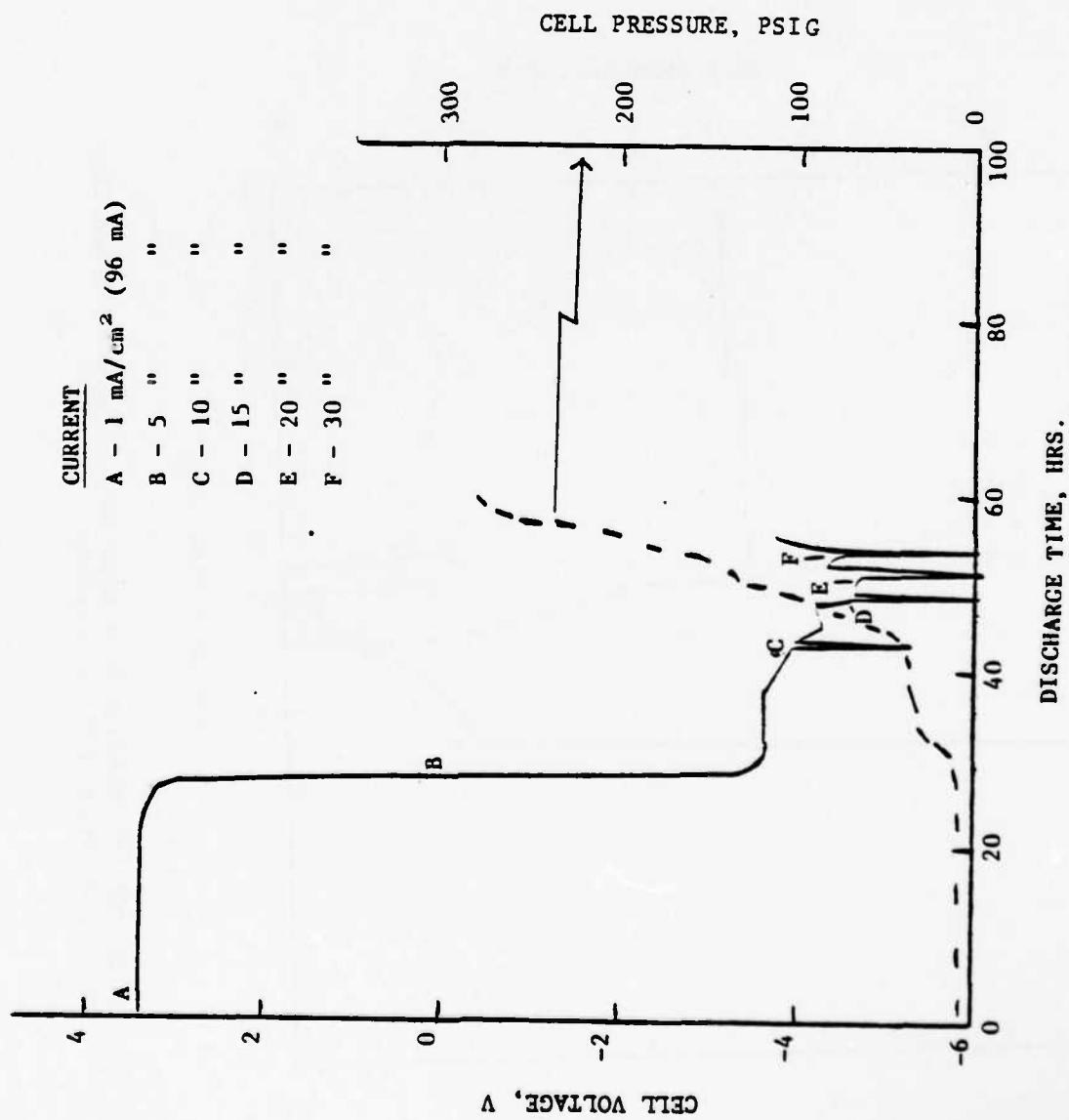
FIGURE 42. DISCHARGE AND REVERSAL OF ANODE-LIMITED BASELINE LAB WRAP CELL.

64
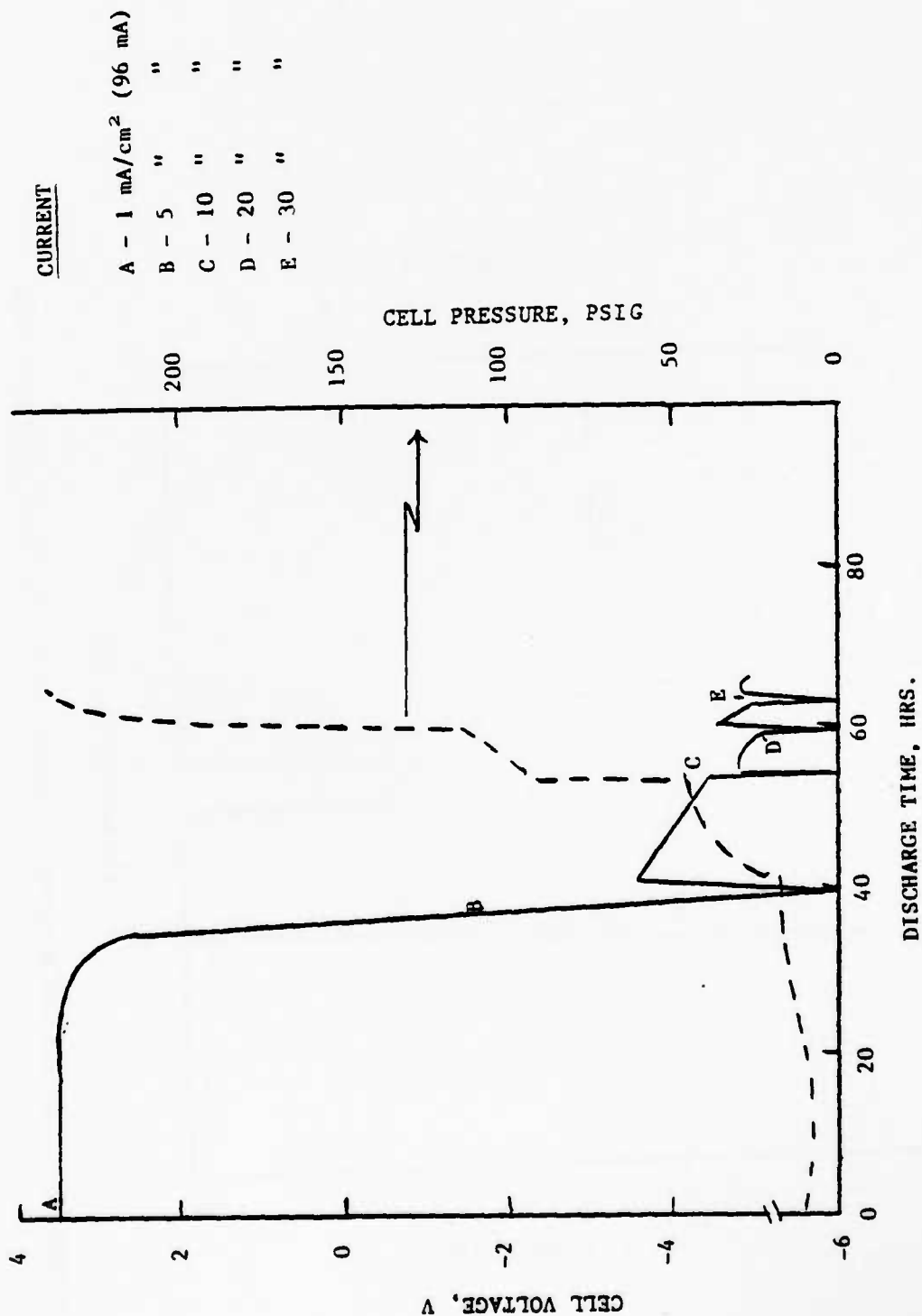
FIGURE 43. DISCHARGE AND REVERSAL OF 7% $(CoPc)_n$ ANODE-LIMITED LAB WRAP CELL CONTAINING 1.25g OF LITHIUM.

CURRENT

A - 1 mA/cm² (96 mA)
B - 5 "   "
C - 10 "   "
D - 20 "   "
E - 30 "   "

65
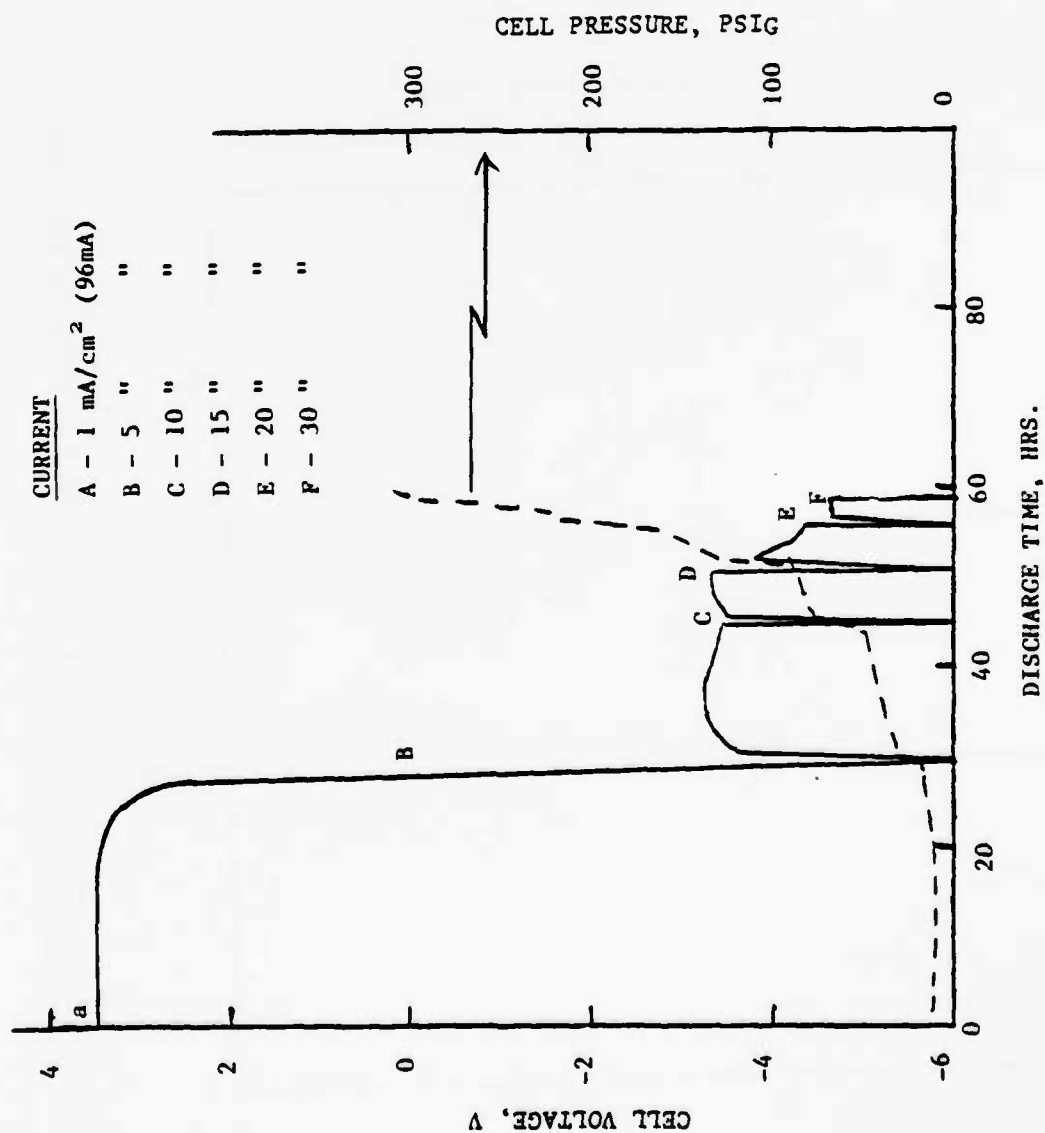
FIGURE 44. DISCHARGE AND REVERSAL OF ANODE-LIMITED, 7% $(CoPc)_n$ LAB WRAP CELL.

66
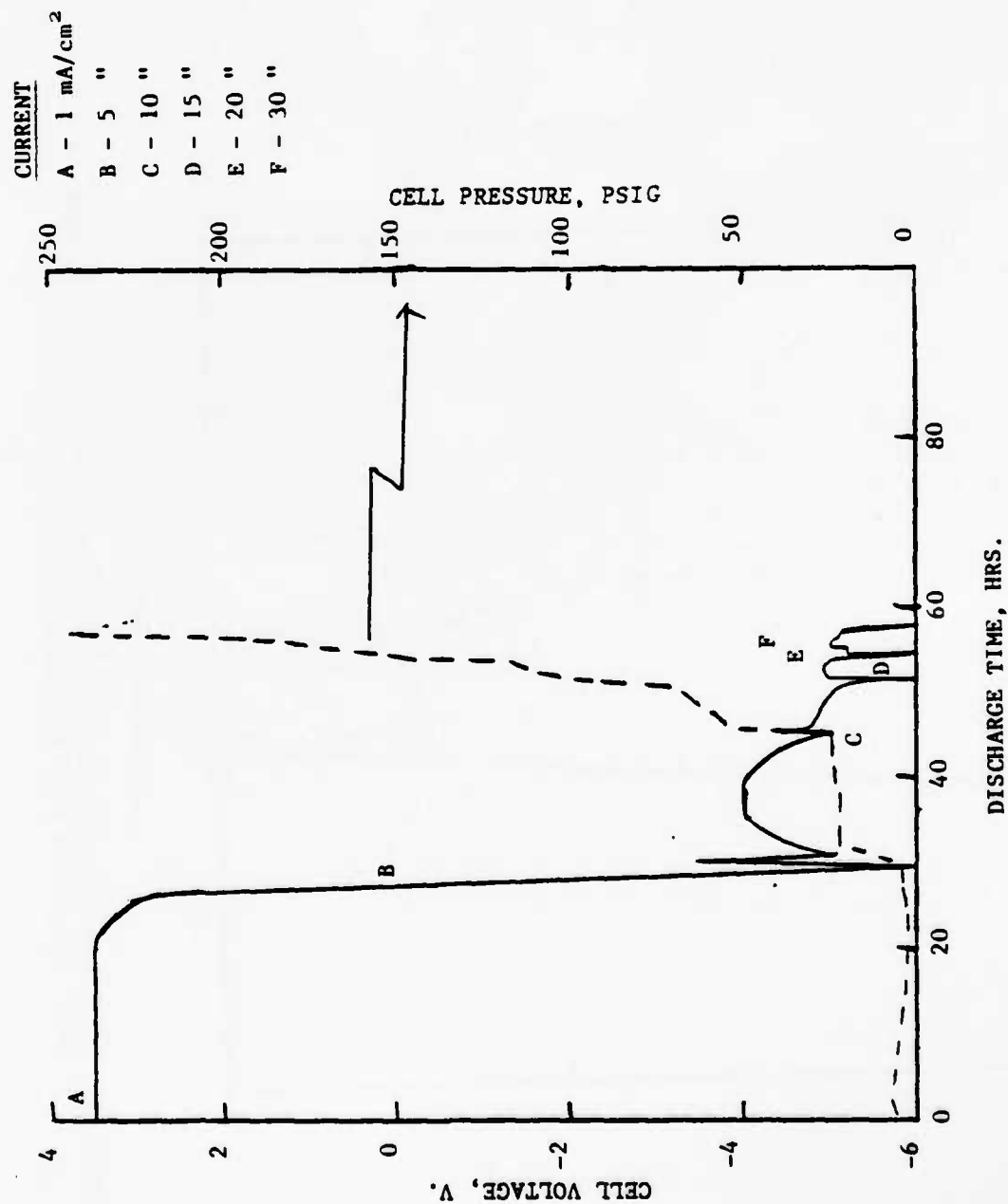
FIGURE 45. DISCHARGE AND REVERSAL OF ANODE-LIMITED, FePc LAB WRAP CELL.

67
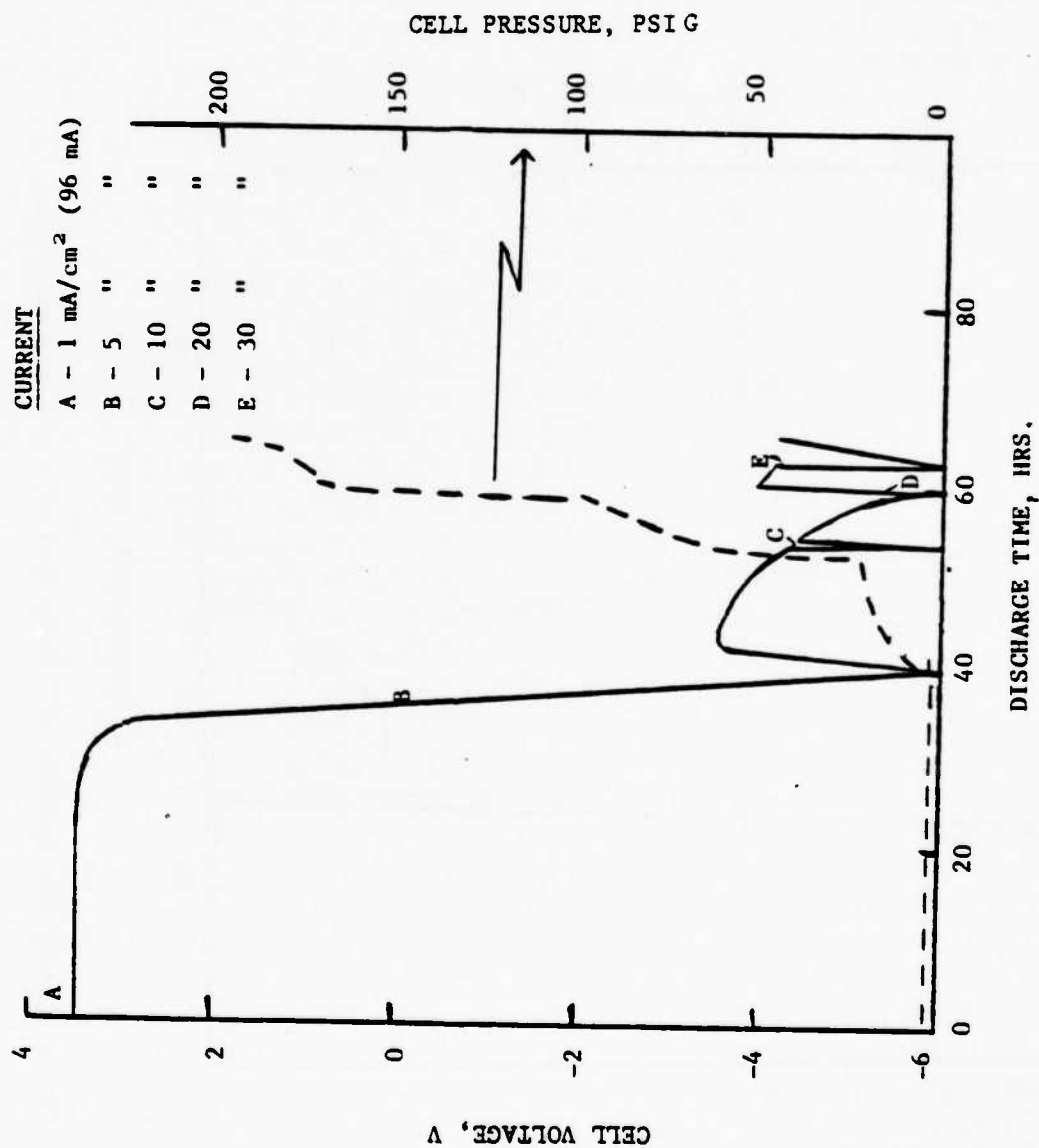
FIGURE 46. DISCHARGE AND REVERSAL OF 1.5% TsFePc, ANODE-LIMITED, LAB WRAP CELL CONTAINING 1.25 g OF LITHIUM.

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Cathode

Dimensions:[*]	1.75" x 4.5" x 0.040" (first piece)
	1.75" x 4.0" x 0.040" (second piece)
Area:	96.0 cm^2
Volume:	9.75 ml
Weight:	3.7 - 3.9 g
Void Space:	81.85% baseline cathode
	(i.e., 0.8185 x 9.75 = 7.98 cc)
	82% $(CoPc)_n$ cathode
	(i.e., 0.81 x 9.75 = 7.90 cc)

Stainless Steel Grids

Dimensions:	1.75" x 3.6" x 0.010" for anode
	1.75" x 3.9" x 0.010" for cathode

Separators - Manning Non-Woven Glass Mat

Dimensions:	2.0" x 8.5" x 0.005"
No. pieces used/cell:	4
Volume:	2.786 ml
Porosity:	90%
Void Space:	0.9 x 2.786 = 2.51 cc

Electrolyte - 1.5M $LiAlCl_4/SOCl_2$

Amount:	20 ml/cell

Cell Case - Compatibility Glass Tube

Volume:	32 ml

[*] Cells 19-21, Cathodes = 1.75" x 5.25" x 0.04" (First piece)
                        1.75" x 4.5" x 0.04" (Second piece)
         Area = 110 cm^2
         Anode = 1.75" x 4.25" x 0.020" (Two pieces)
  Dimensions of separators and grids were also changed accordingly.

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Attachments

Thermocouple (For 12 cells only)
Pressure Transducer
Pressure Relief Valve

Volume: 3 ml

A total of 27 cathode-limited cells with the above electrode desig
and tested. The cells were discharged at constant current of 1 m;
#29-30 at 5 mA/cm^2) with diode protection. The discharge voltage
the pressure of cells without thermocouple (Cell #19 to 33) at th
100% depth of discharge to 0.7 volts is given in Table 6. Slight
in cell-to-cell voltages were observed. This is attributed to tl
treatment and storage conditions. The average discharge voltage
for baseline cathode, 3.48 V for $(CoPc)_n$ catalyzed cathode and 3
catalyzed cathode. The discharge time at 1 mA/cm^2 was 60 hours
71 hours for $(CoPc)_n$ catalyzed cells and 57 hours for FePc cata
catalyst does not improve life at 1 mA/cm^2 rate but does at 5 m;
for this behavior is that FePc undergoes decomposition on longe
$SOCl_2$. Because of the catalytic ability of FePc to improve cel
the achieved power is still higher at the low rate discharge.
catalyst seems to modify the reaction mechanism whereby no gas
to form. This results in lower cell pressure.

After discharge to 0.7 V, the diodes were removed and cells we
forced overdischarge into reversal at various rates. Their d;
in Table 7. Cells 19-21 showed erratic behavior during force
three cells differed from the other cells in that they had mo
electrode stacks. The behavior of other cells with reduced ε
to be identical with and without electrolyte insoluble (CoPc
them sustained forced overdischarge current density of 20 mA
100% depth of discharge time. However, FePc catalyzed cells
. current density of 30 mA/cm^2 during forced overdischarge.

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Table 6. Discharge Performance of Cathode-Limited Cells

Cell #	Catalyst	Rate, mA/cm^2	Discharge Time to 2.0 V,(Hrs)	Cell Volt Voltage	Pressure 100% DOD
19*	-	1	57	3.36	-
20*	$(CoPc)_n$	1	74	3.38	20
21*	-	1	57	3.02	16
22	$(CoPc)_n$	1	73	3.30	31
23	FePc	1	58	3.50	16
24	-	Mechanical Failure			
25	-	1	66	3.37	16
26	$(CoPc)_n$	1	65	3.10	24
26	$(CoPc)_n$	1	73	3.47	17
28	-	1	60	3.06	14
29	-	5	8.6	3.02	7
30	FePc	5	11.2	3.28	6
31	-	1	65	3.38	23.5
32	FePc	1	56	3.53	15
33	$(CoPc)_n$	1	71	3.48	14

* Contained only one layer of separator and a longer electrode stack.

Table 7. Forced Overdischarge of Cathode-Limited Cells Into Reversal

Cell #	Catalyst	Overdischarge Rate (mA/cm²)	Cell Voltage, V	DOOD, * %	Pressure at the End of Overdischarge, psig	Remarks
19	-	0.5	-.10	105	TEF	Leak
		1.0	-.2	91	"	"
		2.0	-.2	100	"	"
		5.0	-.5	100	"	"
20	(CoPc)ₙ	0.5	-1.2	50	39	Cell voltage, erratic. discontinued
21	-	0.5	-.2	150	30	Cell voltage, erratic. discontinued
22	(CoPc)ₙ	5.0	-.36	200	64	Cell vented
		5.0	-.36 → 5.0	12	>100	
23	TsFePc	5.0	-.16	500	43	
		10.0	-.4	400	48	
		15.0	-.8	200	61	
		20.0	-1.3	500	96	
		20.0	-1.3 → -5.0	5	>100	Cell vented
25	-	5.0	-0.2	200	47	Cell vented
		10.0	-0.6	1100	108	
		15.0	-1.0	100	120	
		15.0	-1.0 → -5.0	10	>150	
26	(CoPc)ₙ	5.0	-2.4	72	52	Stopped before voltage dropped below -7.0V
		7.0	-3.5	280	65	
		10.0	-4.3	360	>100	
27	(CoPc)ₙ	5.0	-0.10	170	25	Forced overdischarge Discontinued when voltage dropped below -5.0V
		10.0	-0.15	550	32	
		15.0	-0.20	600	36	
		20.0	-0.32	720		
		20.0	-0.32 → -5.0	320	100	
28	-	1.0	-0.35	50	23	Forced overdischarge discontinued
		10.0	-0.76	700	33.5	
		15.0	-1.05	800	42	
		20.0	-1.40	1280	47.5	
29	Was disassembled after discharge and analyzed for electrochemically consumed lithium					
30	" "	" "	" " "	"	" "	
31	-	10.0	-0.5	100	31	Discontinued
		20.0	-1.2	720	65	
		20.0	-1.2 → -6.0V	580	>180	
32	FePc	10.0	-0.3	100	35	Cell exploded
		20.0	-0.6	1100	75.5	
		30.0	-1.0	100	>280	
33	(CoPc)ₙ	10.0	-0.55	100	21	Voltage dropped below -5.0V
		20.0	-1.10	200	>100	

* Depth of Overdischarge

The cell pressure increases slightly (except for FePc cells) during discharge and the increase accelerates for all cells when overdischarged and depends upon the rate. Cell failure was usually accompanied by a spontaneous spike in pressure beyond 200 psig and sharp voltage drop.

All cells were postmortemed after overdischarge. It was noticed that at the end of overdischarge, lithium was completely consumed leaving bare stainless steel grids. The products formed during cell reversal seem to react with lithium. It is interesting to note that this finding contradicts the reported data in which it was reported that lithium either deposits or intercalates with carbon in the cathode during cell reversal. Our data show that free lithium does not exist probably due to its consumption by chemical reactions with cell reversal products.

In order to further examine the thermal behavior of cathode-limited cells during discharge and forced overdischarge into reversal, wrap cells were built with thermocouple, pressure transducer and vent valve. The temperature of the cell at the center of the wrap was measured with an Omega type-T thermocouple. In Figures 47-52, the temperature, pressure and voltage behavior of wrap cells are presented. Irrespective of cathode types [i.e., undoped cathode, FePc or $(CoPc)_n$ doped cathodes], the cells either exploded or vented under forced over-dischrge current rate of 30 mA/cm^2 after 1-5 hours. The cell failure is preceded by a sudden increase in both temperature and pressure. The temperature, pressure and voltage behavior of these cells six to seven minutes prior to the cell failure are given in Figures 53-56. All have shown similar characteristics. It can be concluded that the thermal runaway conditions are created during cell reversal. Further, the current density and cell design appear to influence the thermal behavior. Even in the case of the cathode-limited design, the amount of lithium left after discharge seems to influence the cell safety as shown in Figures 57 and 58. The low sustaining current rate capability of these cells might be due to depletion of lithium at an early stage and therefore drop in voltage causing severe heat generation. However, the anode-limited cells experienced higher temperatures without causing cell explosion.

73
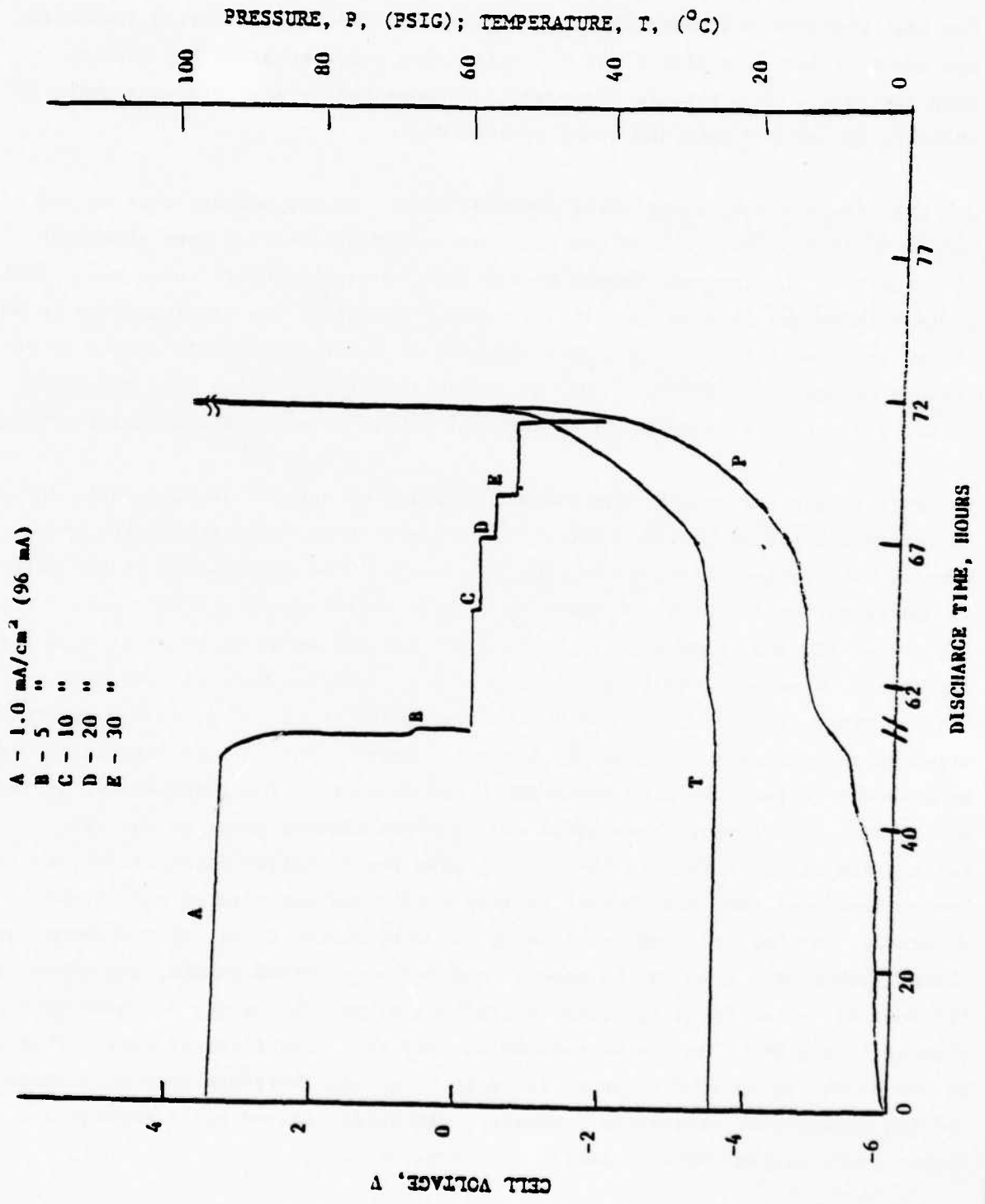
FIGURE 47. DISCHARGE AND OVERDISCHARGE CHARACTERISTICS OF LI/SOCl₂ WRAP CELLS WITH BASELINE CATHODE AND 1.5M LiAlCl₄/SOCl₂ ELECTROLYTE AT 23°. ANODE THICKNESS 0.013"
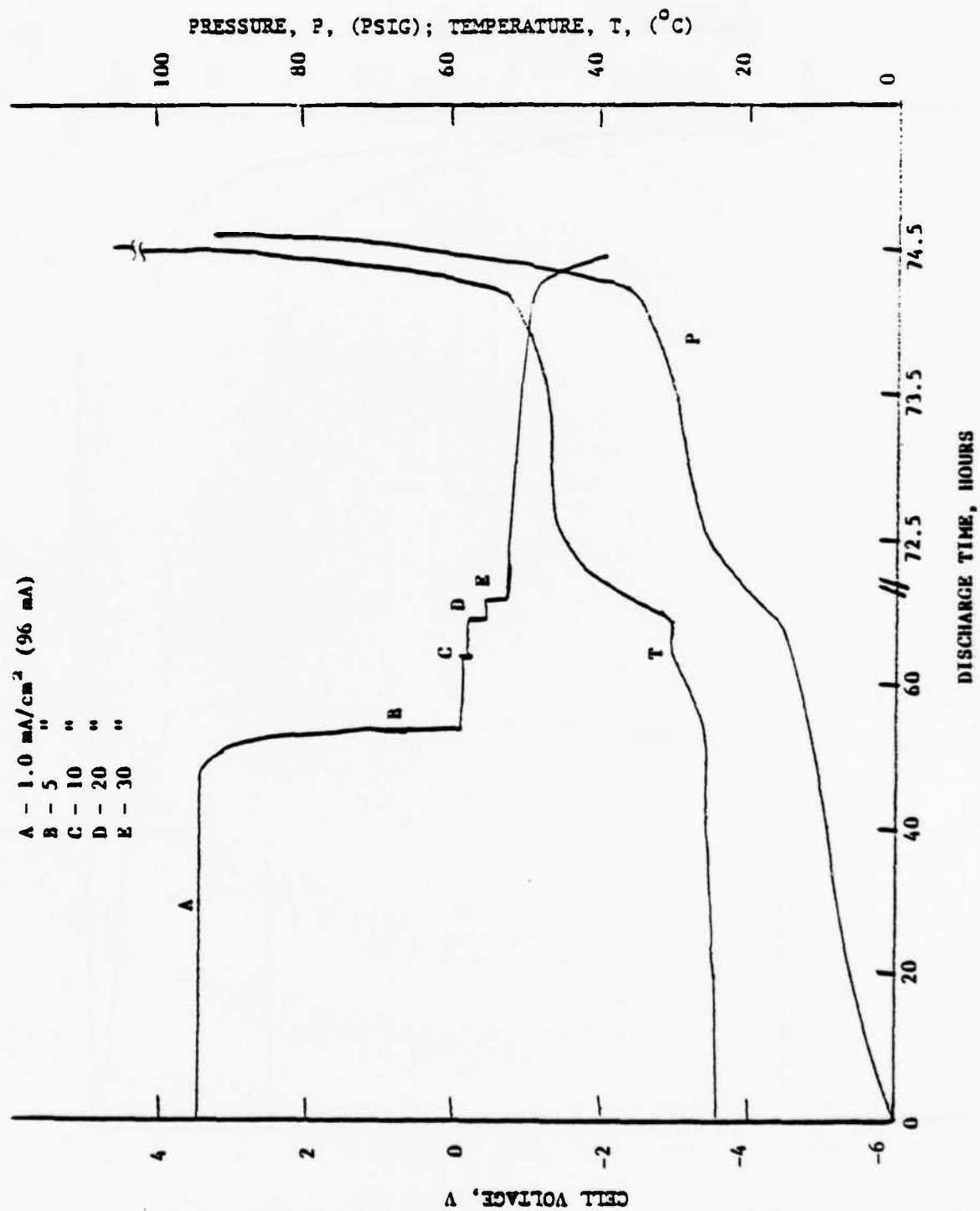
FIGURE 48. DISCHARGE AND OVERDISCHARGE CHARACTERISTICS OF Li/SOCl₂ WRAP CELLS WITH (CoPc) CATHODE

75
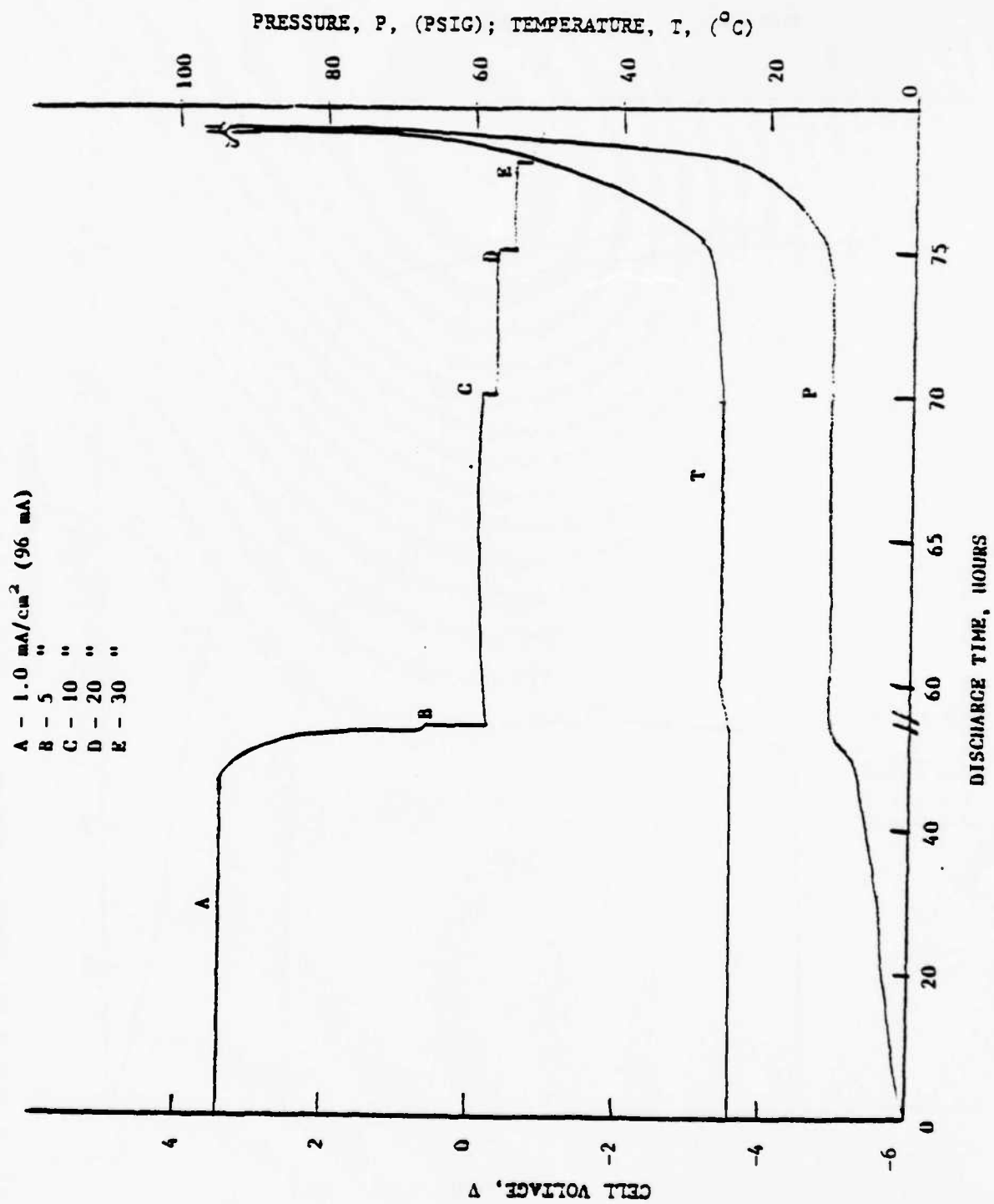
FIGURE 49. DISCHARGE AND OVERDISCHARGE CHARACTERISTICS OF Li/SOCl$_2$ WRAP CELLS WITH ((CoPc) CATHODE

PRESSURE, P, (PSIG); TEMPERATURE, T, (°C)

100   80   60   40   20   0

A – 1.0 mA/cm² (96 mA)
B – 10   "
C – 20   "
D – 30   "

(Recorded only
during reversal)

72   67   62   40   20   0

DISCHARGE TIME, HOURS

4   2   0   -2   -4   -6

CELL VOLTAGE, V

77

FIGURE 51. DISCHARGE AND EXCESS OVERDISCHARGE CHARACTERISTICS AT EACH OF THE 5 RATES

78
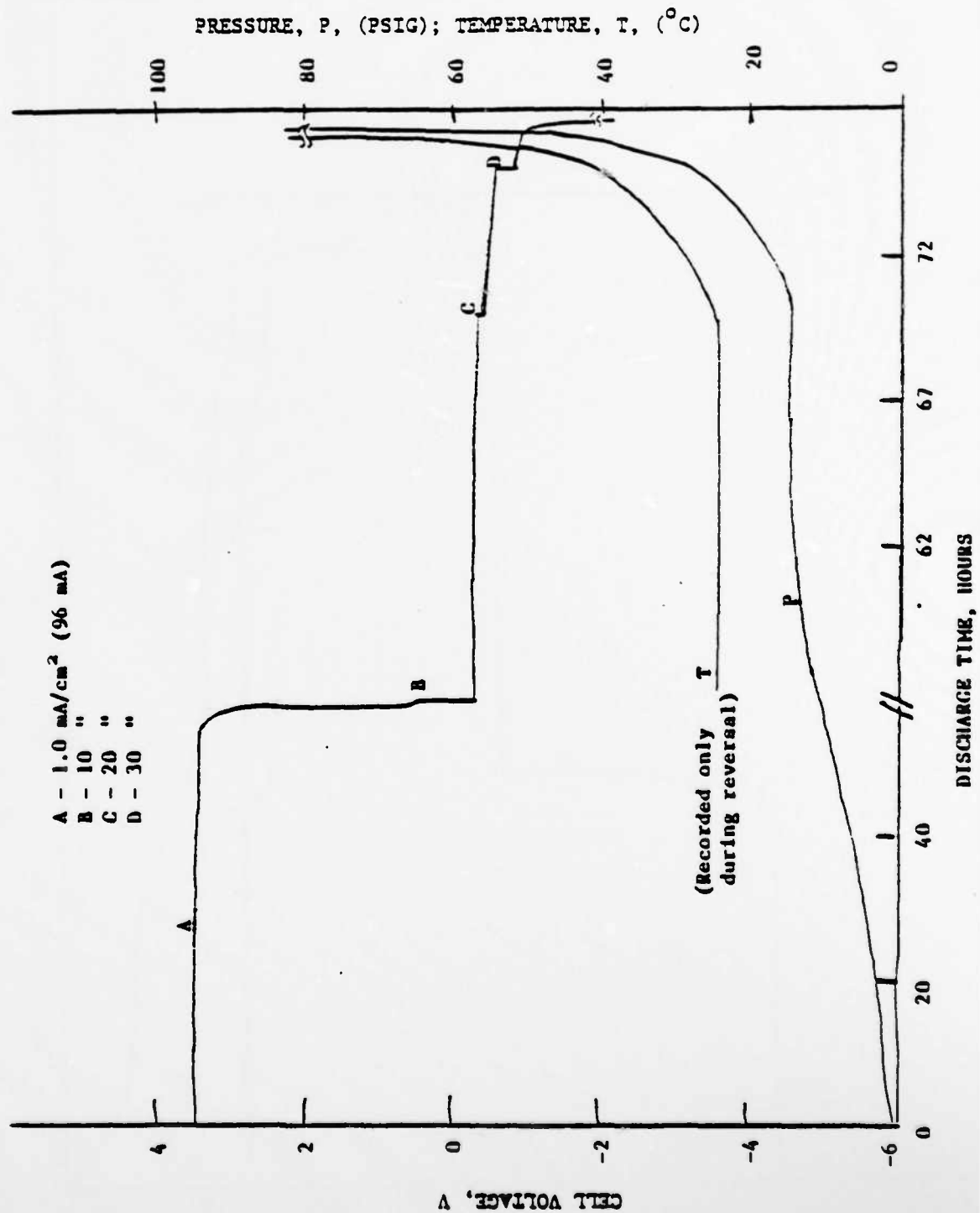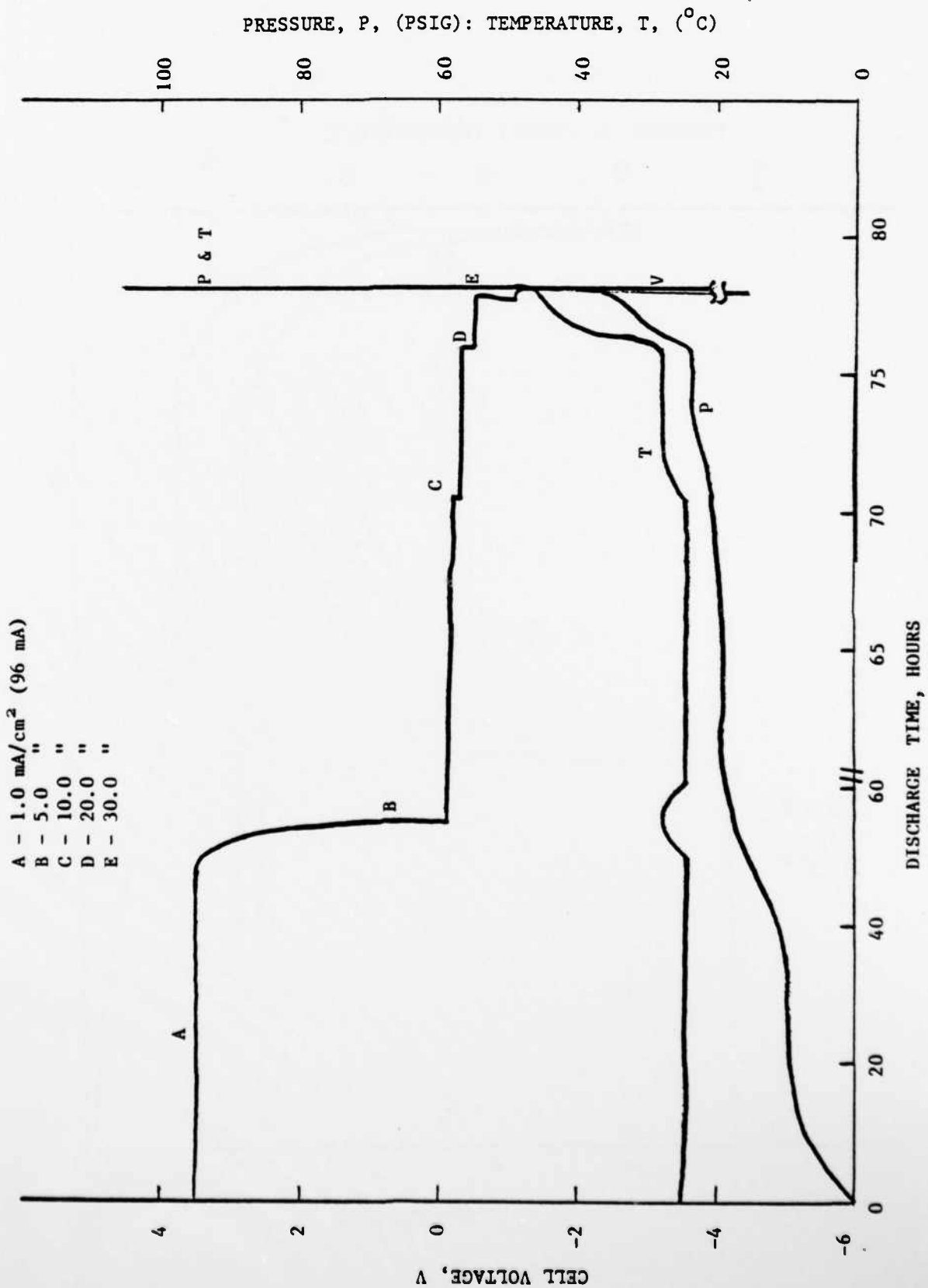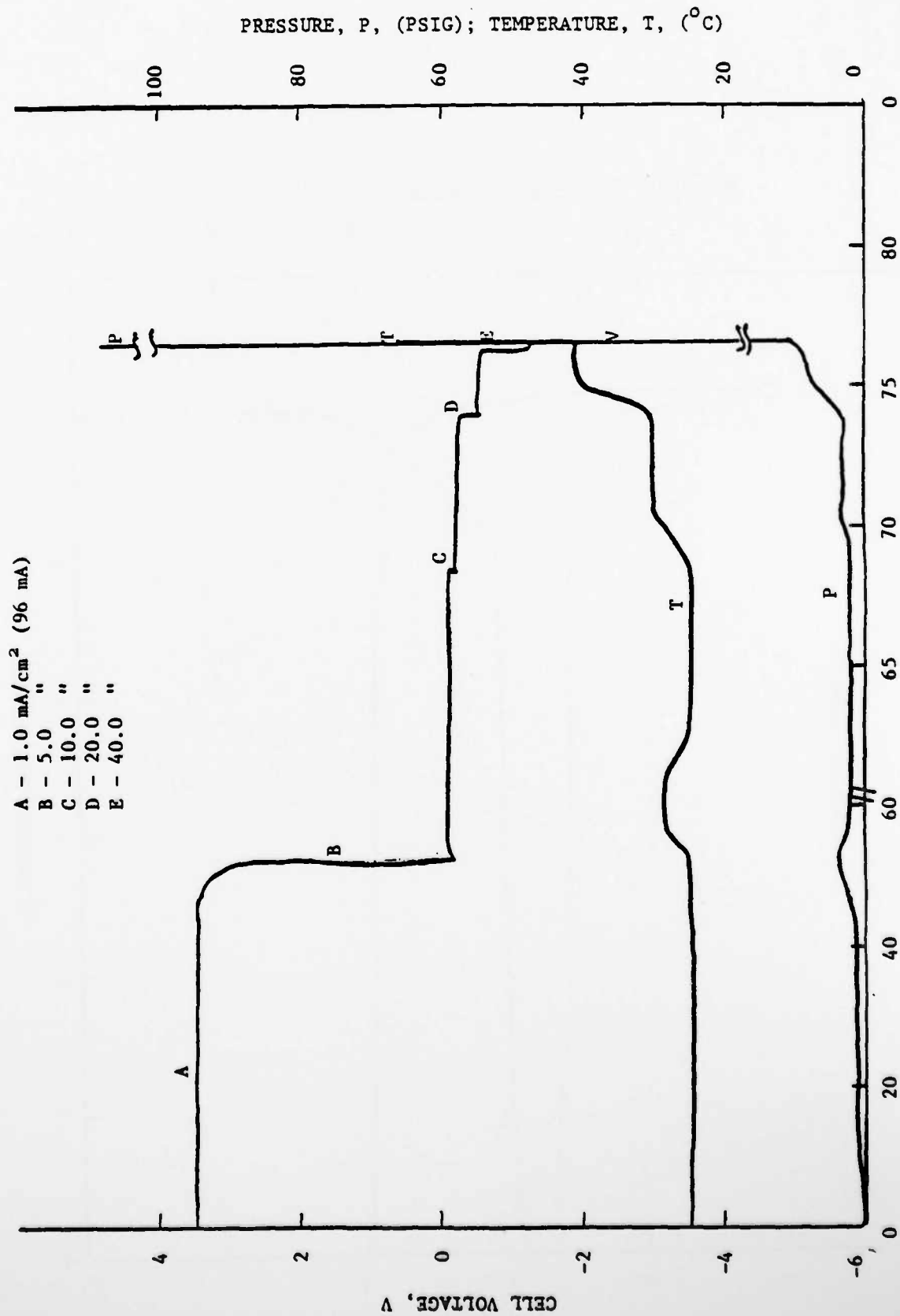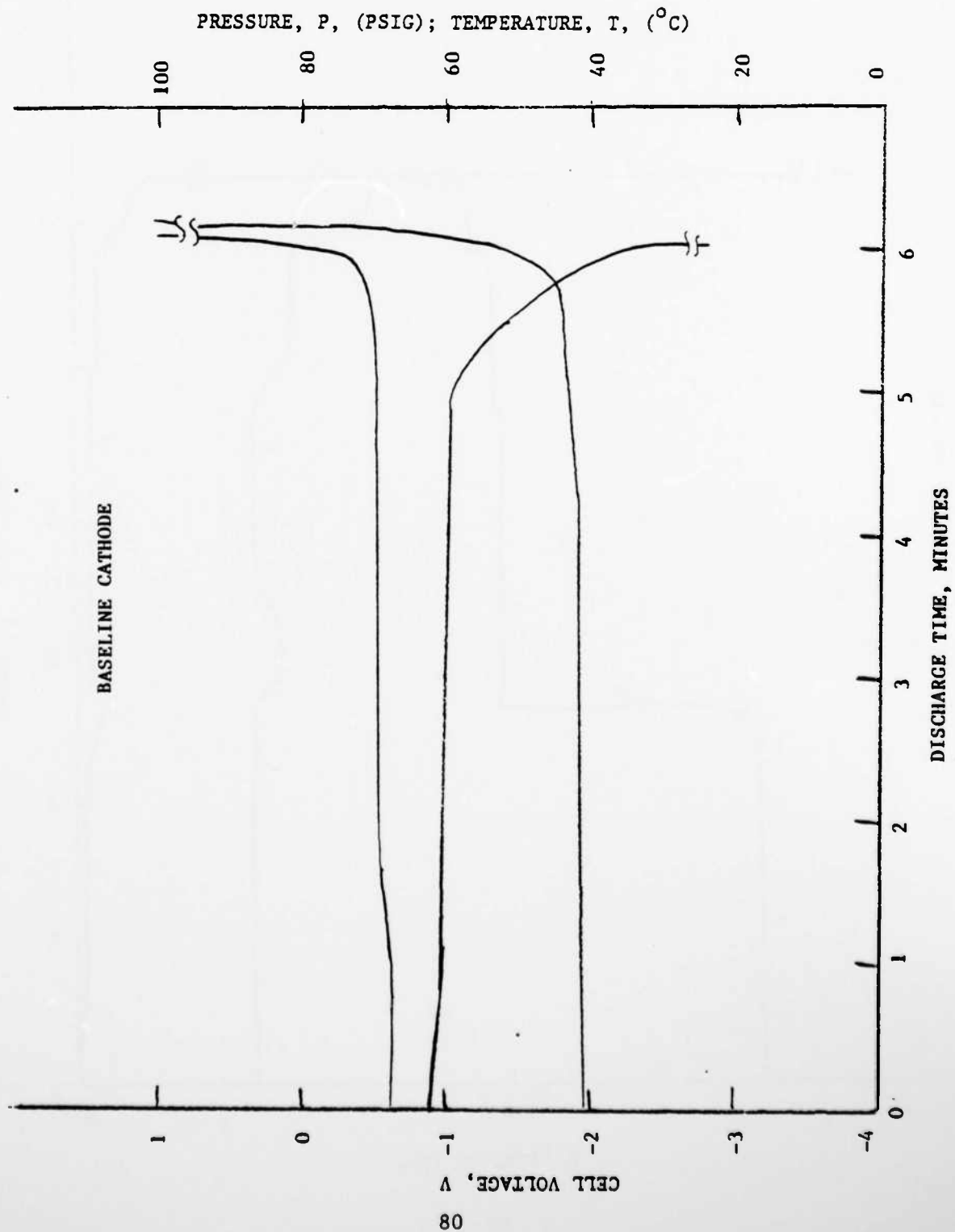
FIGURE 53. VOLTAGE, PRESSURE AND TEMPERATURE BEHAVIOR OF Li/SOCl₂ UEAR CELLS PRIOR TO HEAT DISSIPATION

BASELINE CATHODE

PRESSURE, P, (PSIG); TEMPERATURE, T, (°C)

CELL VOLTAGE, V

DISCHARGE TIME, MINUTES

PRESSURE, P, (PSIG); TEMPERATURE, T, (°C)

$(CoPc)_n$ CATHODE

0.040" THICK ANODE

DISCHARGE TIME, MINUTES

CELL VOLTAGE, V

82

PRESSURE, P, (PSIG); TEMPERATURE, T, (°C)

$(CoPc)_n$ CATHODE

0.040" THICK ANODE

DISCHARGE TIME, MINUTES

CELL VOLTAGE, V

83

PRESSURE, P, (PSIG); TEMPERATURE, T, (°C)

DISCHARGE TIME, HOURS

CELL VOLTAGE, V

A - 1.0 mA/cm² (96 mA)
B - 5 " "

85
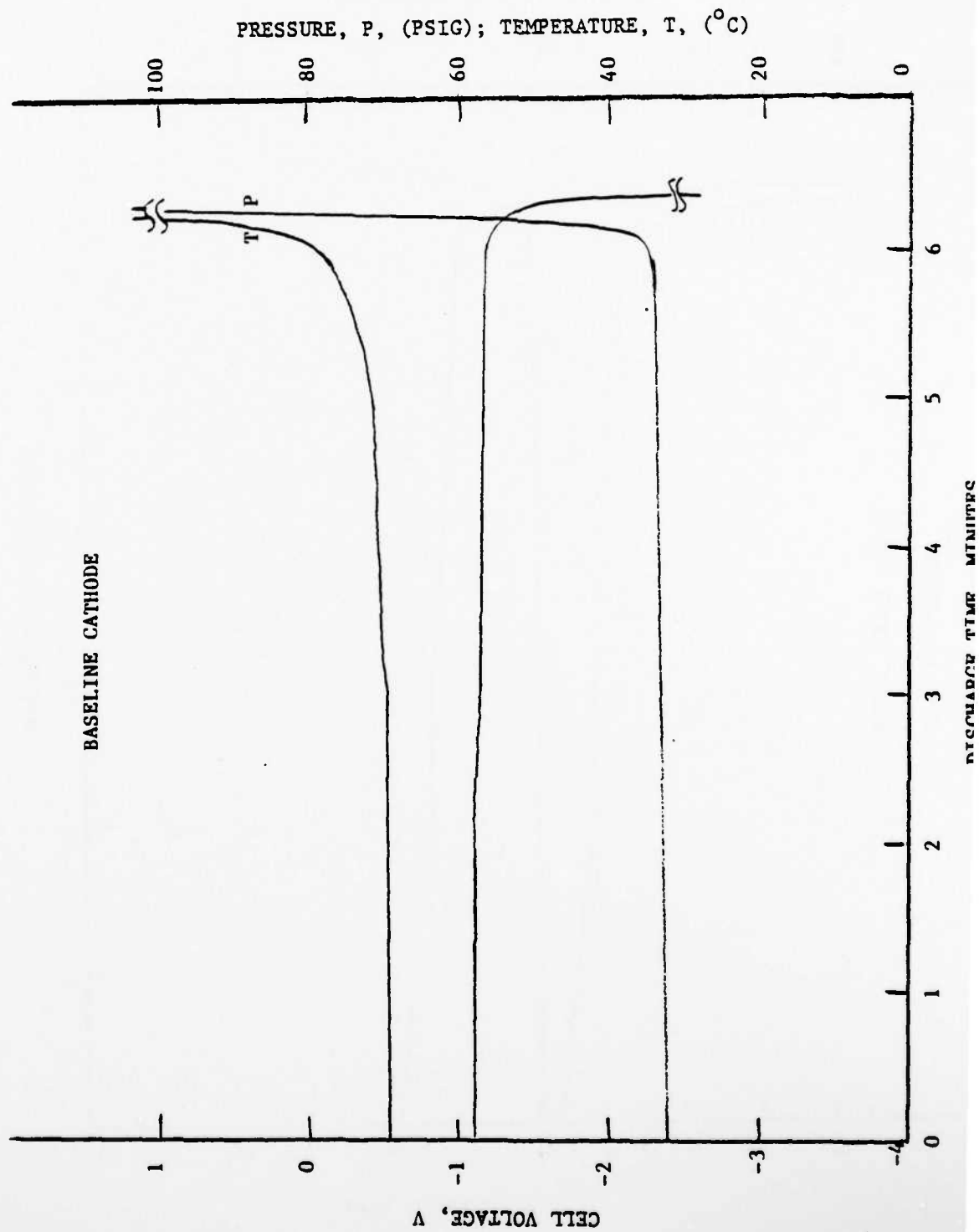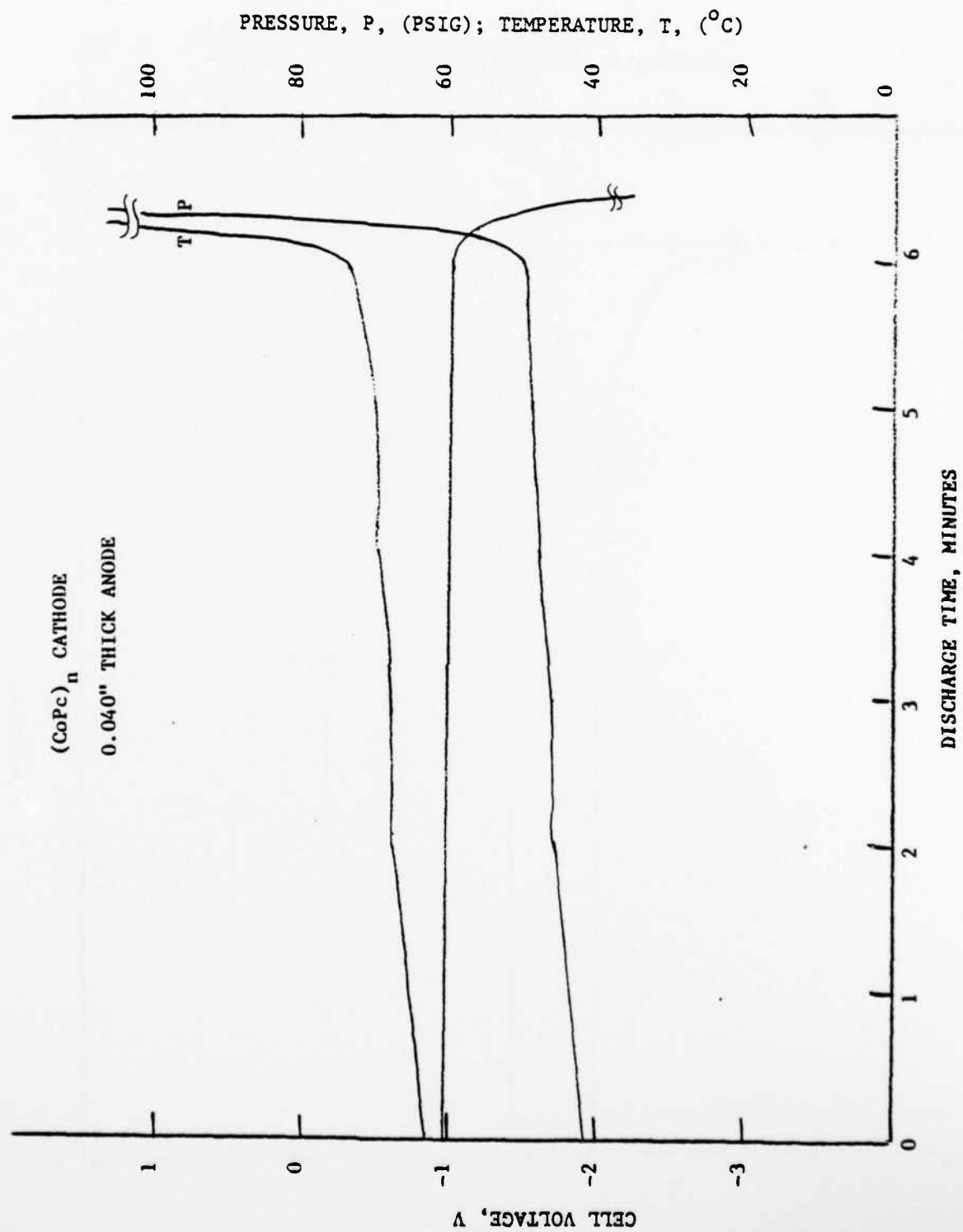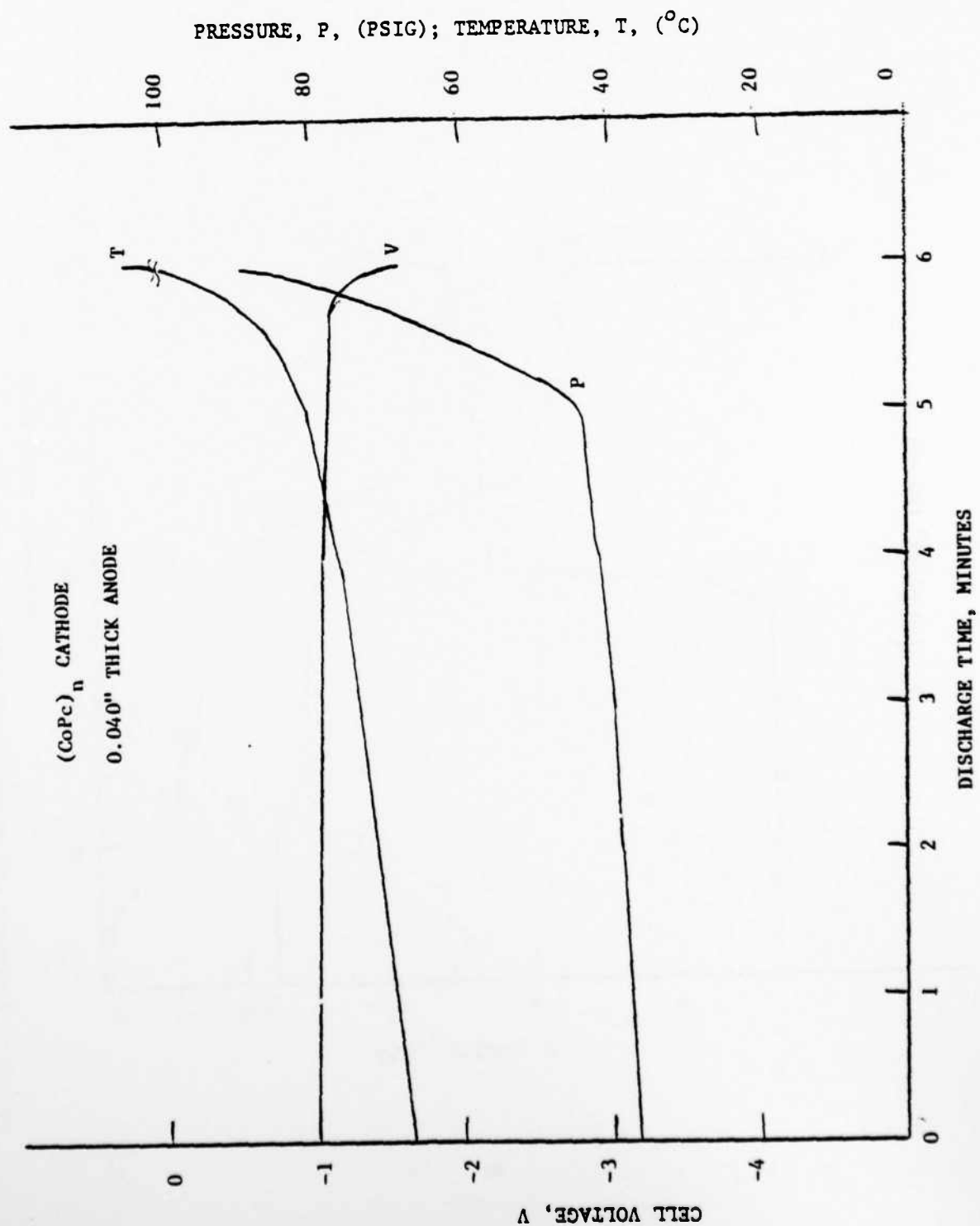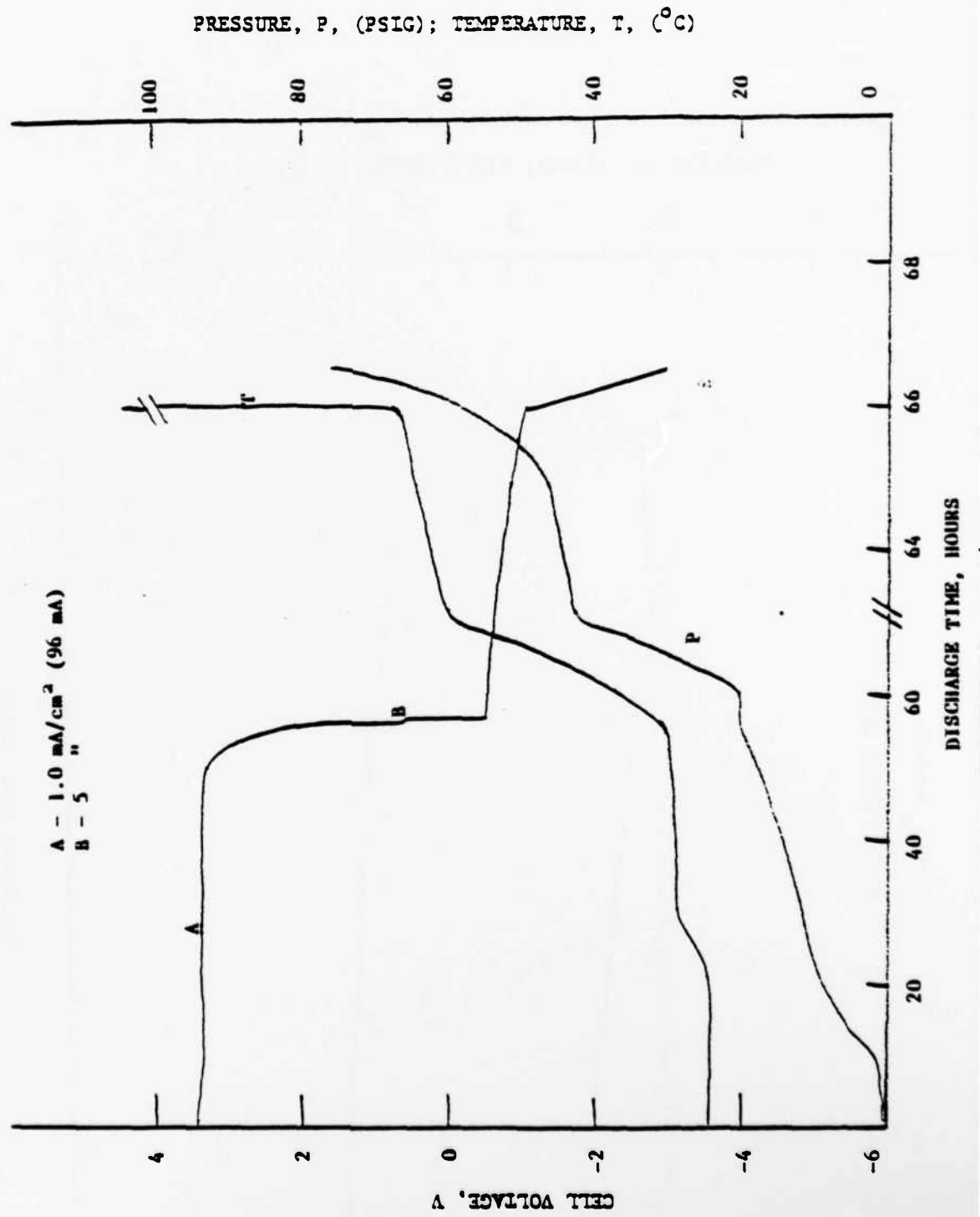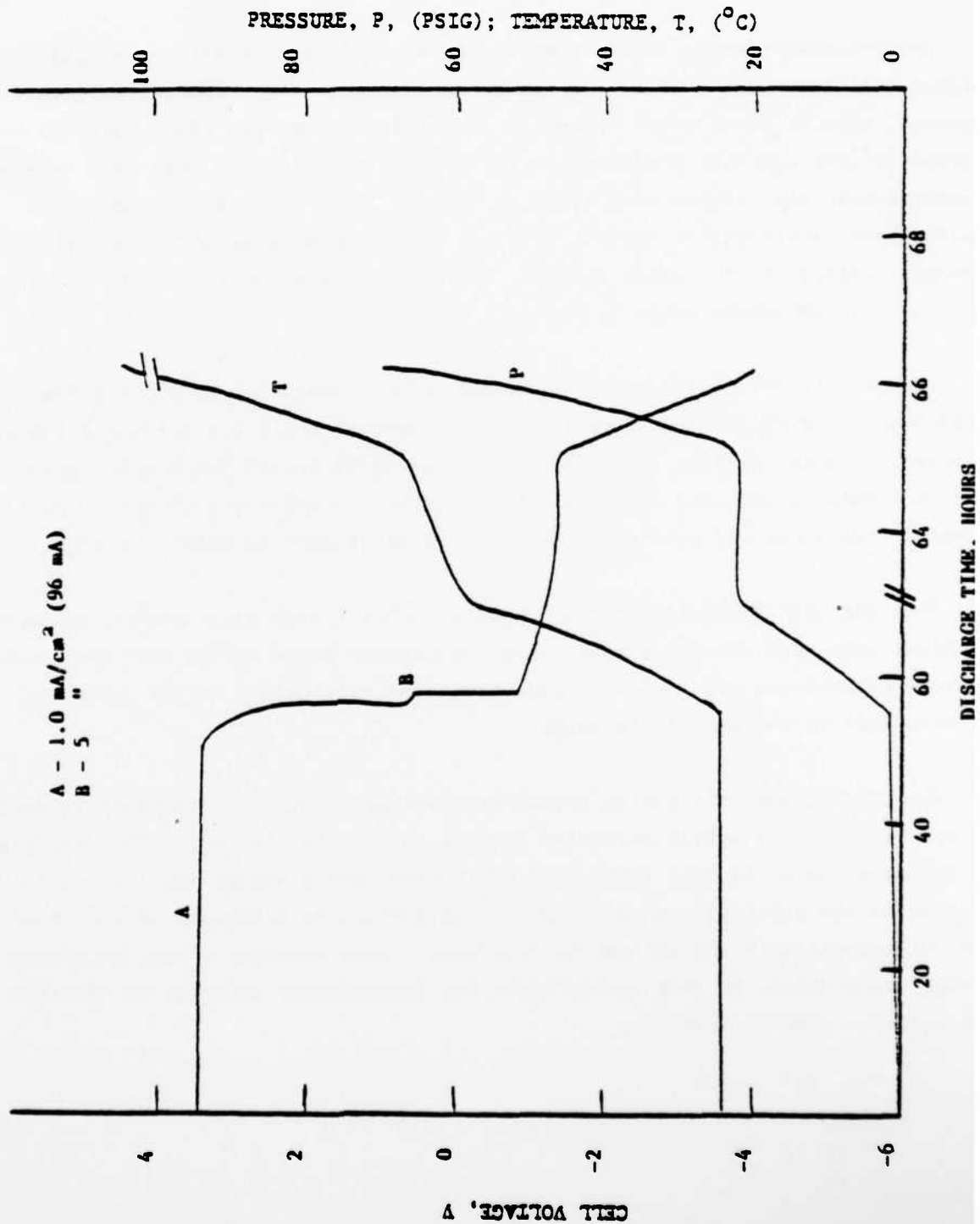
In summary, it can be said:

•   Anode-limited design cells experienced severe heat generations leading to higher cell pressures even at low current densities during reversal studies. However, none of these cells vented or exploded. Postmortem after reversal studies showed lithium dendrite formation on the cathode surface. At high cell reversal temperatures, the lithium dendrites, if formed, could be consumed chemically. Furthermore, the reactive species produced under these conditions could also undergo changes leading to new stable species. Therefore, care should be taken to interpret the reaction mechanism based on analysis of products.

•   Cathode-limited design cells sustained current densities up to 20 mA/cm^2 for 100% depth of overdischarge into reversal. However, all cells exhibited sudden increase in both pressure and temperature leading to either venting or explosion. The cell failure appeared to be related to thermal runaway conditions. Both chemical reactions and cell shorting could cause unexpected safety hazards.

•   When the cathode-limited design cells were built with only slightly excessive lithium, they were able to sustain very low current rates during cell reversal. Further experiments are needed to understand the cell safety on the amount of lithium left at the end of discharge.

•   The product analysis during forced overdischarge into cell reversal is needed to understand the reaction mechanism leading to the cell failure. The analysis of products has to be done throughout the forced overdischarge into reversal to examine the critical concentration of the product or products, if any, that are participating in the exothermic reactions. Cell reversal of anode-limited design cells should be done at low operating temperatures in order to identify the unstable species produced.

5.0 MISCELLANEOUS STUDIES

ELECTROCHEMICAL

Elucidation of kinetic and reaction mechanisms of thionyl chloride reduction with and without electrocatalysts such as CoPc, and FePc is important to understand the role of intermediates and/or final products. It was shown that CoPc and FePc not only catalyze the electrochemical reduction rate of $SOCl_2$ but also modify the reaction mechanisms. In Figure 59, the cyclic voltammograms at a pressure annealed pyrolytic graphite in 1M $LiAlCl_4/SOCl_2$ electrolyte with and without catalysts are shown. At a fresh and dry electrode surface, two reduction peaks are obtained without catalyst. With the addition of metal free phthalocyanine complex, the reduction peaks merged and peak current increased threefold. If monomeric cobalt phthalocyanine, CoPc, is added, the peak shifts to more positive potential. Furthermore, the cyclic voltammograms with catalysts do not contain reduction or oxidation peaks beyond 2.0 V.

Addition of SO_2 to the electrolyte without catalyst generate a reduction peak at 2.0 V. However, with CoPc catalyst, SO_2 reduction peak does not appear which could be due to the saturation of the electrode with adsorbed products. Similar results are also observed with the addition of Cl_2. Further studies are needed to identify peak positions of known additives and generate and identify species between 2 and -5 volt vs lithium reference electrode.

FTIR

Studies on the nature of $SOCl_2$ adsorption with carbon cathode with and without catalyst (CoPc or FePc) were initiated by FTIR specroscopic techniques. Preliminary FTIR spectra (Figures 60-62) of $SOCl_2$ with and without catalyst showed no significant variation in peak positions. The electrolyte thickness has to be minimized to study actual adsorbed layers. Further studies to optimize the FTIR cell design experimental conditions are needed.

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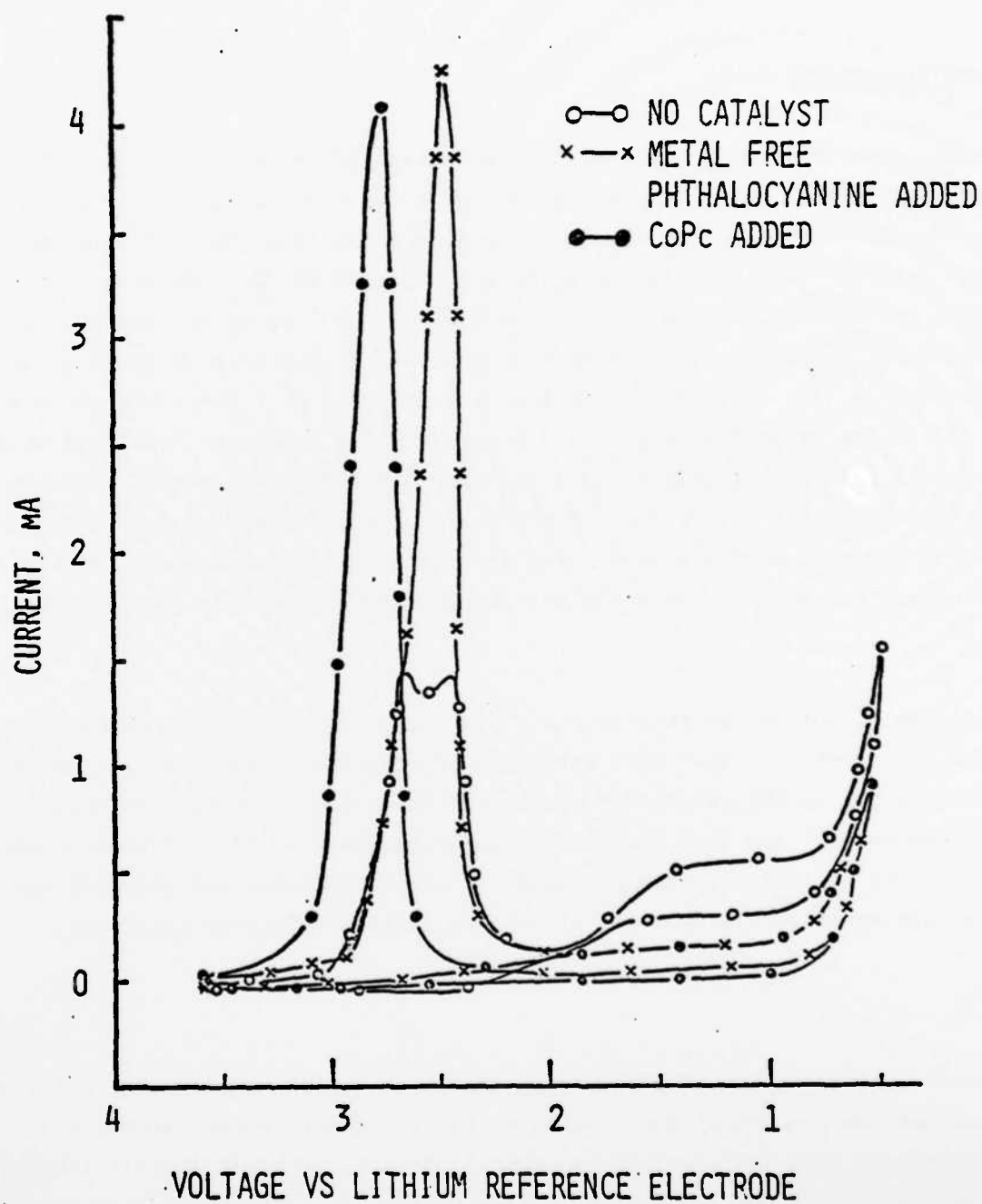
FIGURE 59. CYCLIC VOLTAMMOGRAMS AT PRESSURE ANNEALED PYROLYTIC GRAPHITE
(0.178 cm^2) IN 1M LiAlCl$_4$/SOCl$_2$ ELECTROLYTE. SWEEP RATE
100 mv/sec.

88
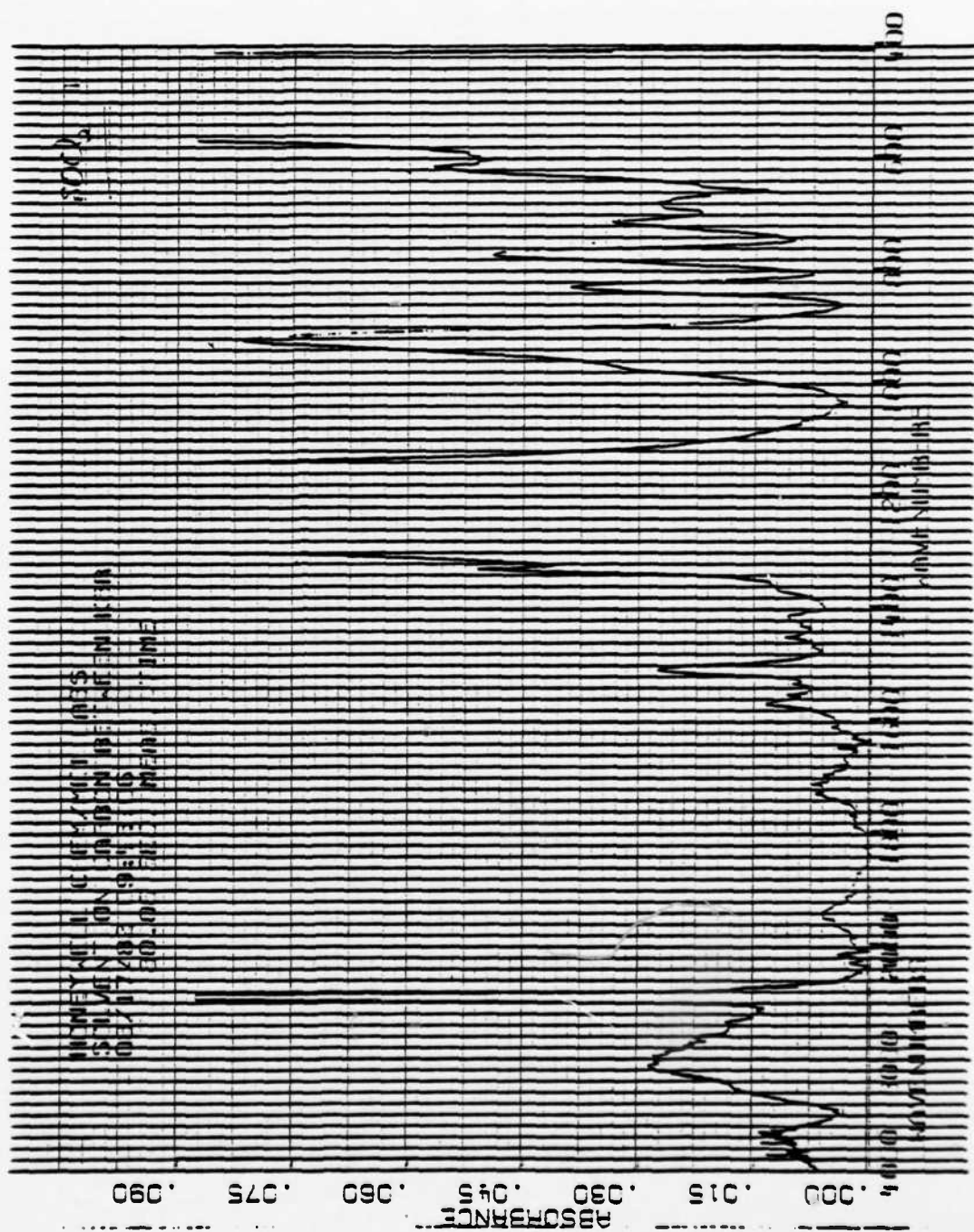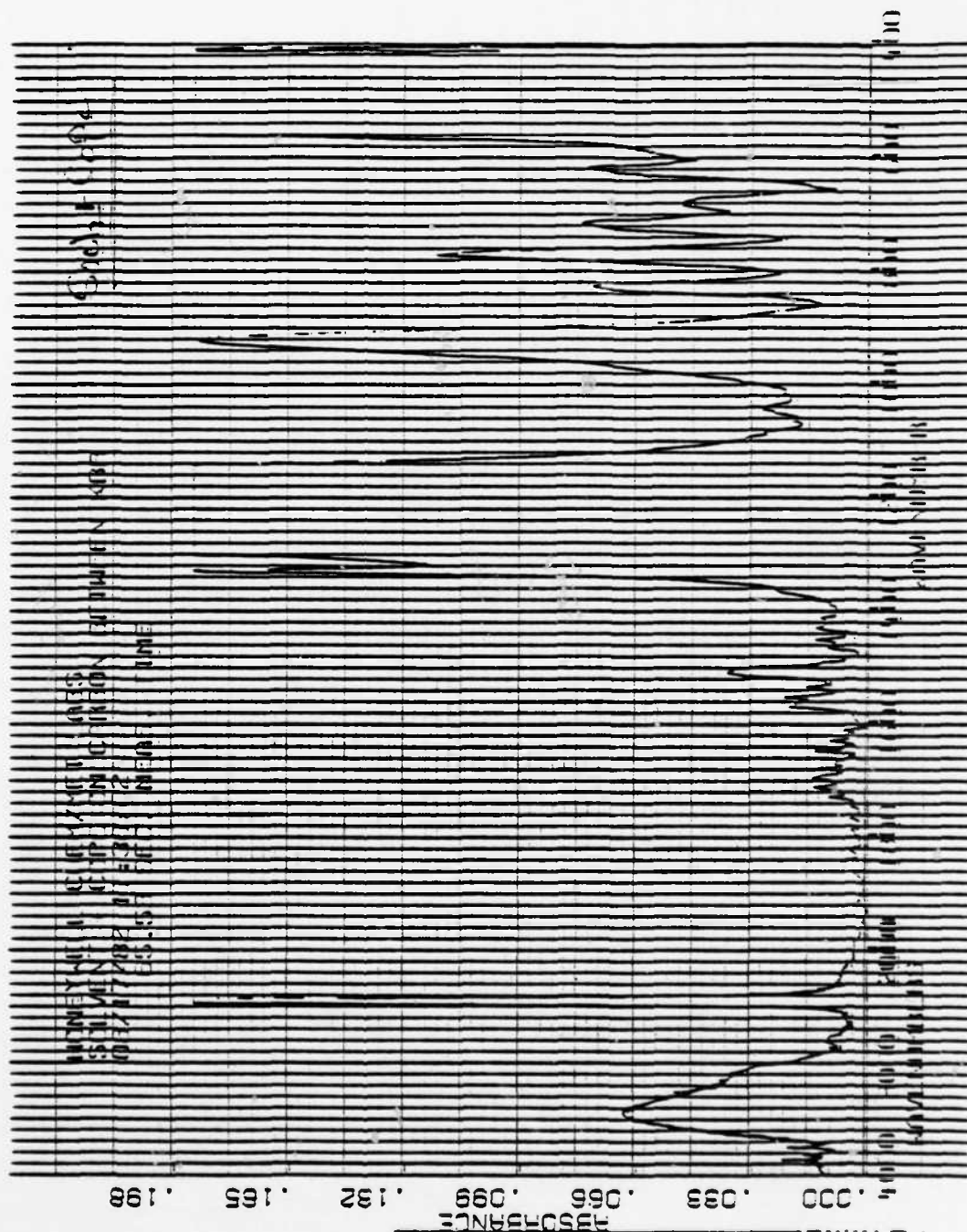
FIGURE 61. FTIR SPECTRUM OF $SOCl_2$ + CoPc ON POROUS CARBON CATHODES
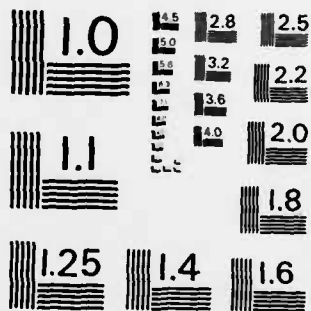
MICROCOPY RESOLUTION TEST CHART

NATIONAL BUREAU OF STANDARDS-1963-A
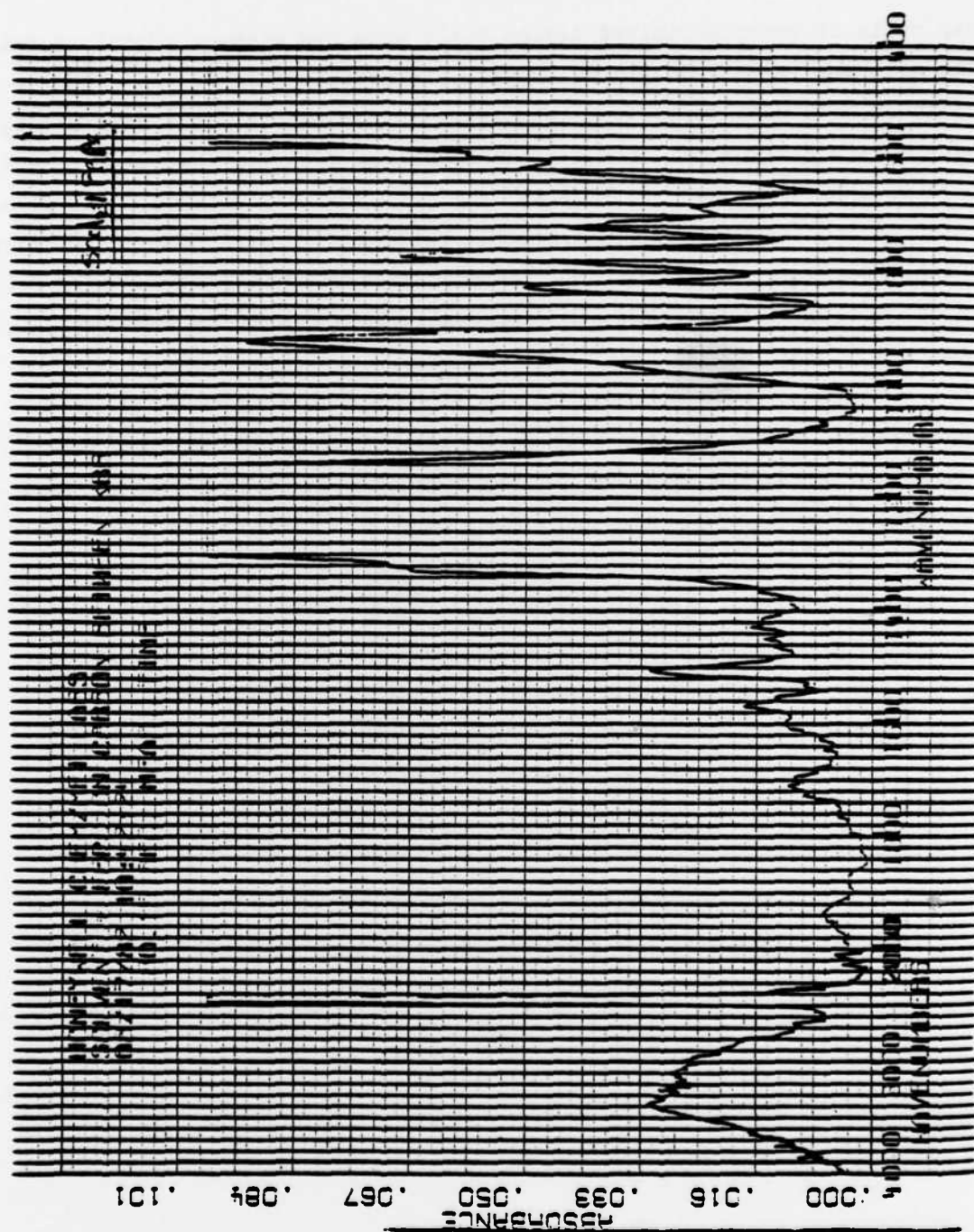
FIGURE 62. FTIR SPECTRUM OF SOCl₂ + FePc ON POROUS CARBON CATHODES

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Li/SO$_2$Cl$_2$ SYSTEM

Wrap cells of cathode-limited design built, with and without (CoPc)$_n$ catalyst, were activated with 1.5M LiAlCl$_4$/SO$_2$Cl$_2$ electrolyte in order to evaluate the effect on both performance and the safety of the system. The data of eight such cells are given in Table 8. The discharge cell life increases nearly by 20% over that of Li/SOCl$_2$. However, the cells failed after only 65% of depth of forced overdischarge into reversal. The cause of cell failure was attributed to the electrical discontinuity. Postmortem of the cells showed both lead wires and anode grid were severely corroded. All cells exhibited pressure spike, temperature rise and voltage drop just before the cell failure. None of the cells, however, either exploded or vented. If stainless steel grids were replaced with nickel grids, the cell reversal time decreases further. Further studies are needed to identify the reactive species produced during reversal and the cause of grid corrosion.

Table 8. Discharge and Forced Overdischarge Characteristics of Li/SO_2Cl_2 Cells with 1.5M $LiAlCl_4/SO_2Cl_2$ Electrolyte at 23^oC

Serial No.	Cathode	Cell and Grid Type	Discharge Time (Hrs) (1 mA/cm^2) (2.0V)	Pressure(psig) at 2.0V	Cell Reversal Time (Hrs) (5 mA/cm^2)	Pressure (psig) Just Before Cell Failure	Voltage (V) Just Before Cell Failure
1	Baseline	Wrap & S.S.	70	40	10.5	58	-0.2
2	Baseline	Wrap & S.S.	69	44	8.5	60	-0.2
3	$(CoPc)_n$ (2)	Wrap & S.S.	72	27	9.0	89	-0.2
4	$(CoPc)_n$ (2) + 0.5 g camphor	Wrap & S.S.	70	40	8.5	>200	0.2
5	$(CoPc)_n$ (2)	Wrap & Nickel	75	26	2.5	74	0.2
6	Baseline	Wrap & Nickel	74	28	-	-	-
7	$(CoPc)_n$ (1)	Wrap & S.S.	75	28	-	-	-
8	Baseline + CoPc 3 mg/cc	Wrap & Nickel	73.5	30	-	-	-

(1) Lithium was complete gone at the end of discharge time.
(2) Postmortem after overdischarge revealed severe grid corrosion; nickel grid was completely disintegrated, whereas th stainless steel grid became thinner (0.01" — 0.005"), also weld joints.

Notes: 1. Maximum temperature recorded at the time of cell failure was 150°F.
2. Pressure spike, temperature raise and voltage drop occur simultaneously.
3. Maximum cell pressure recorded was 110 psig.

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6.0 SUMMARY AND CONCLUSIONS

● Temperature-pressure studies of D-cells showed:

  - No change in final pressure whether or not the cells were subjected
    to heat/cool cycles after various depths of discharges.

  - Maximum cell pressure at the end of 100% depth of discharge at
    1 mA/cm^2 rate were 40 and 100 psig corresponding to 30 and 70°C
    operating temperatures, respectively.

● Long term reservoir storage studies revealed:

  - Stability of $(CoPc)_n$ in 1.5M LiAlCl$_4$/SOCl$_2$ electrolyte.
  - Surface corrosion on 316L and 321 stainless steel specimens.
  - Higher corrosion rates on 321 than on 316L.
  - Higher corrosion rates in acid electrolyte than neutral electrolytes.
  - Initial corrosion film inhibits or reduces further corrosion.

● Forced overdischarge into cell reversal studies showed:

  - $(CoPc)_n$ catalyzed cathodes improved cell voltages and did not show
    adverse effects on the behavior of cells during forced overdischarge.

  - Cathode-limited design cells sustained current densities up to
    20 mA/cm^2 for 100% of nominal cell capacity during forced overdischarge
    into cell reversal. However, these cells showed unpredictable venting
    or exploding behavior, thus making them less attractive. Further, the
    current sustaining rate capability decreased when cells were built with
    lesser amounts of lithium. Based on the data of a few experiments
    carried out, it appears that balanced cells might be much more dangerous.
    than cells having either anode-limited or cathode-limited design.
    In all cases, the cell failure appears to be related to thermal runaway
    conditions.

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Anode-limited cells sustained higher current densities (20 mA/cm^2) than cells of cathode-limited design. These cells experience severe heat generations leading to high cell pressures during cell reversal. However, none of the cells with optimized electrode stacks either vented or exploded. Reactive chemical species or lithium dendrites formed during discharge and forced overdischarge into cell reversal, if any, seemed to undergo changes leading to the formation of stable species at the high temperature environment in anode-limited design cells. Therefore, we believe that cells of anode-limited design are much safer under abuse conditions such as those described in NAVSEA's Instruction 9310.1A.

- **Fundamental Studies**

    - Further electrochemical and non-electrochemical (FTIR) studies, with and without catalysts, are needed to identify the reactive species produced and the nature of SOCl$_2$ adsorption.

- **Li/SO$_2$Cl$_2$ System**

    - Li/SO$_2$Cl$_2$ cells produced longer discharge life. Severe anode corrosion due to parasitic reactions was also observed during discharge.

    - Future forced overdischarge into cell reversal, both nickel and stainless steel grids and lead wires, were severely corroded. Grid and lead wire corrosion appears to lead to the electrical discontinuity. During normal discharge, grid and lead wire corrosion was not observed. During studies are needed to understand the cause for the grid and lead wire corrosion.

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